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An Introduction to
CHEMICAL SCIENCE

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CHEMICAL SCIENCE

SECOND EDITION

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PREFACE

This edition of *An Introduction to Chemical Science* follows the general plan of the first edition. The division into four parts—inorganic, organic, food and industrial chemistry—has proved useful to more than one kind of student, although these four parts were and are intended to form a continuous study for non-specialists.

The course of study for which this book has been written is not a survey of the physical and biological sciences. I believe that of all the sciences chemistry lends itself best to the inculcation of basic scientific principles inherent in all sciences and to the applications of modern science as they touch most frequently and intimately the lives of our people. Consequently the correlation with the other sciences is stressed only in so far as it tends to develop a scientific mode of thought and a solid acquaintance with the development of chemistry in all its commoner phases.

Most of the features of the first edition are retained here. Each chapter has its summary and a list of questions, the latter considerably enlarged. The treatment is still in the main historical. The chapter on atomic structure is deliberately delayed until the reader has acquired sufficient acquaintance with chemical properties and electricity to make the reading intelligible.

In Part 1 the new features include a chapter (Chapter 3) devoted to the properties of matter, the inclusion of nitrogen in the study of the atmosphere (Chapter 5), a more thorough treatment of gases (Chapter 6), a chapter on atomic and molecular weights (Chapter 10), a chapter on electrolytes (Chapter 14) and a more detailed study of metals and alloys (Chapter 18).

Part 2 has been enlarged to provide more information (Chapter 26) on modern pharmaceutical and related substances.

Part 3 remains much as it was, except for more recent information on the vitamins.

Part 4 has undergone a definite change in plan to conform to the raw materials from which chemical products are obtained. Addi-

tional information of a general nature has been included, notably a chapter on plastics (Chapter 39) and another on cooking (Chapter 40).

These new features have occasioned rearrangement, especially in Part 1, where the Periodic Classification of the elements has been so treated as to make Chapter 17 unnecessary if more time is required in Part 4. Almost all production figures have been omitted; in the world at present no such figures can be considered either complete or useful.

Although I have found the sequence of topics presented here to be the most suitable for my own classes over the years, I do not suggest that it is the best one. Such a decision as well as the decision regarding lecture demonstrations and laboratory experiments (if any) must of course be left to the individual instructor. The development of a sound appreciation of chemistry and of science in general is not subject to academic or other regimentation.

W. H. Hatcher

McGill University
December, 1948

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Finally I wish to acknowledge permission from the Canadian Legion Educational Services to include some material not present in the first edition.

W. H. H.

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Part 1

INORGANIC CHEMISTRY

1

In the Beginning

1 Out of Chaos

The story of science is merely one aspect of the story of man, who in the course of the ages has sought to subdue nature for his protection, for his greater comfort and for the expression of his own individuality through the gratification of his innate curiosity. This is as true of the human race as a whole as it is of the various civilizations, which, rising and falling, gave place to others in that seemingly endless progression we call history.

The formation of our earth was probably due to the slow change of a nebulous body of hot gases, thrown off by the sun, into a more or less solid mass or shell of material covered by water and a gaseous envelope of air. The slow cooling of these hot gases caused the formation at first of liquid masses in constant motion, and finally of solid masses, whose compositions differ so widely that seams and pockets of vastly unlike materials are found below the earth's crust. The kaleidoscopic nature of this crust has been further accentuated, even since the relatively late appearance on the earth of vegetation and animal life, by such surface catastrophes as volcanic eruptions, earthquakes, landslides and glacial erosion. Obviously life could have appeared only after cooling had produced conditions favorable for growth and, it is believed, in simple forms at first. Though evolutionary changes resulted in a further complexity of matter at the surface of the earth, considerable complexity was present originally in the atmosphere (a mixture of several gases), in the water (which contains many dissolved substances) and in the crust of the earth itself. The advent of life merely increased the complexity of nature. Actually very few substances are found existing free, that is, in a pure state; examples are gold, platinum and diamonds.

2 And Then Man

The appearance of man probably meant little in history, beyond the universal search for food and the consequent destruction of the many for the benefit of the more intelligent few. Man, however, developed the power of speech to a greater degree than his lower associates, and so was able to communicate a record of his actions and thoughts to his fellows. Thereafter legends grew from generation to generation, to be succeeded in relatively recent times by the carved and then the written word; the last method, though not infallible, has the advantage of simplicity and accuracy over the previous records. Thus the development of the civilizations known to history can be traced where such records exist. It should not be assumed, however, that no civilization superior to the present (from the point of view of scientific achievement) has ever existed because no record of it exists. One really large sunspot or long ice age, with its attendant effects on the earth's crust, could remove thoroughly all trace of present-day civilization.

What has been discovered from the records of the past indicates that the last two centuries have seen the development of more creature comforts, a higher degree of medical knowledge and more efficient methods of destruction than have previously been known. Against this must be set an increasing amount of proof that China, Asia Minor and Central America may have attained, centuries ago, many of the present-day objects by parallel, even if not identical, routes. Whether today men of the highest intellectual stature are mentally superior to the philosophers of, say, the five centuries preceding the Christian Era is still open to doubt.

3 Metal versus Stone

The earliest man, in order to sustain life, made his implements of stone; crude but efficient metallurgical operations produced the implements of the later Bronze Age. The invention of steel manufacture (probably in India) coincides with the beginning of the modern age. The steel swords of Damascus and, centuries later, of Toledo were famous for their strength, flexibility, temper and endurance. The legions of Julius Caesar, with their short sharp swords, were superior in equipment to the Britons under Boadicea, whose chariots were equipped with bronze scythes which were capable of being bent by a strong breeze. The Spaniards of Cortez easily overcame the warriors of Mexico, whose armament was

mainly of pure gold and silver. The metallurgy of iron and steel is the backbone of modern engineering practice—hence the international anxiety for iron supplies.

The transition from the Stone to the Bronze Age was accomplished by harnessing fire, the explanation of which was not forthcoming until the end of the eighteenth century.

The only connected story of civilization as we know it today probably had its beginnings about 6000 B.C. in Asia Minor. The early Chaldeans were followed by the Assyrians and Babylonians, who showed great engineering skill in their building and irrigation projects along the Tigris and Euphrates, and developed the most fertile soil and finest crops ever recorded. How much of their arts was original with them and how much acquired by way of the trade routes to China and India are matters for conjecture.

4 Ancient Arts

The civilization of Crete in the later Bronze Age rivals that of Egypt, and the voyages of the Phoenicians brought to the east metals from the mines of Africa and Spain and even from far-away Britain. Evidence exists to show that chemistry as an art has existed for more than thirty centuries, but has been a science for not more than one-twentieth of that time. As an art it probably antedates astronomy, whereas mathematics as a science early developed many systems, whose uses varied according to the pursuits of the peoples concerned. Astronomy, the study of the heavenly bodies, taught the dwellers of Mesopotamia to decide upon the most favorable times for seeding and harvest; in Egypt mathematics took the form of geometry, the measurement of surfaces, since properties frequently lost their boundaries during the Nile inundations; the Greeks used mathematics for speculations on the behavior of the heavenly bodies, thereby concluding that nature works according to fixed laws; and to the Phoenicians mathematics was the calculation of commercial exchange and of navigation.

The early blending of astronomy, religion and chemistry is evident from the naming of certain metals after the sun, moon and planets, which likewise were national gods. Even in modern times inexplicable natural phenomena are often referred to as celestial intervention in terrestrial routine.

As early as thirteen centuries before Christ the Egyptians were proficient in the chemical art, which then comprised metallurgical processes. The hieroglyphics of these people have left permanent records for succeeding generations, owing to their custom of embalming their important dead.

5 Greece Starts Thinking

The Golden Age of Greece produced (500 to 300 B.C.) a great number of scientific speculators whose main deficiency was their lack of interest in practical experimentation as we understand it. Thus Thales of Miletus considered water the beginning and end of all matter; Anaxagoras spoke of invisible seeds of matter, anticipating the idea of atoms and molecules; Leucippus postulated the existence of space; Democritus conceived of atoms of the soul, the inhalation of which provided life. During this period in Greece the pure science of mathematics made phenomenal advances, perhaps independently of the progress made by the Hindus at about the same time. Also, for the first time in history, a treatise was written (by Theophrastus) describing five hundred varieties of plants and suggesting the existence of sex in that kingdom. The written works of Aristotle on mathematics and biology are a monument to the great achievement of the Greek philosophers in the realm of knowledge.

Lack of scientific experimentation prevented any exact contribution to chemistry. However, names were given the so-called elements—earth, air, fire and water, symbolic of the units of chemistry today; and the Greeks even then had the idea that these elements composed matter by the mutual attraction of atoms in the ether medium.

6 An Exodus of Mind

The subjugation of Greece by Alexander the Great in 330 B.C. and the rise of Alexandria in Egypt shifted the center of learning to that city for the next seven centuries. There arose the greatest library of ancient times, and science made great strides through the genius of Archimedes, Ptolemy and others. The decline of Alexandria began in the first century with its conquest by the Romans, who, though skilled in highway and military engineering, did not emulate the achievements of the Greeks.

7 Alchemy Comes to Europe

Nomadic pressure from the northeast having weakened the Roman hold, Alexandria fell in A.D. 641 to the Arabs, who in one short century crossed the north littoral of Africa into Spain and were stopped only at Poitiers by Charles Martel. At Cordova they established a university, combining the elements of science from Hindu, Greek and Egyptian sources into an advanced study which came to be known as *alchemy*. Baghdad was known as a center of chemical manufacture, as well as of medical practice. Unfortunately for the advance of chemistry, the Moslem mind tended rather to the mystical and occult than to the practical. To this greatest period of Spanish scientific history the contributors were chiefly Jews and Moslems. In spite of persecution their knowledge persisted, though they themselves disappeared under the pressure of their northern enemies.

The name *chemistry* has several possible roots, but the most probable one has reference to the black soil of Egypt, where it flourished for nearly twenty centuries. Hence chemistry was frequently called the Black Art and, by implication, witchcraft.

8 Alchemistic Ideals

By this time we find followers of the Black Art, known as alchemists, working toward one or more of three goals: (1) to discover the philosopher's stone, one of whose virtues was to change base metals into gold (for the theory was that all such metals were sick and could by suitable treatment, called transmutation, be made well, that is, into gold); (2) to prepare the elixir of life, which would cure all human ills and perhaps prolong life indefinitely; and (3) to discover a universal solvent, or alkahest. In the light of present knowledge it is pathetic in the extreme to see what almost superhuman efforts, what huge fortunes and how much earnest faith were dissipated in the struggle to attain these objectives.

The first goal was determined not so much by man's greed as by the firm hope of being able to obtain, by a royal road, that most precious medium of exchange, gold, for which robber barons pillaged and murdered, leaving desolation in their wake.

The search for the elixir of life, the second objective, was a part of the stirring fight against the devastating plagues of the Middle Ages which spared neither rich nor poor. These are two chapters

in the history of alchemy which are replete with noble aspirations, undying faithfulness to the hitherto unattainable and a pathos only comprehensible in the light of the awful conditions of the poor of those times.

The third objective was essentially chemical—the discovery of a substance with the ability to dissolve all the refractory materials encountered by the alchemist, no thought, however, being given to the question of a container for this solvent.

Out of these labors were developed better methods for old operations, new processes for the preparation of metals and their compounds, the beginnings of modern pharmacy, the precursor of modern chemistry, and the highly developed art-science of medicine.

9 Names Which Live

It is difficult to portray the emergence of chemistry as a science in a direct line because of the contributions of other sciences over a long period of time. The principles of the scientific method as first enunciated by Aristotle were given emphasis by Roger Bacon, a Franciscan friar, in the thirteenth century and by Sir Francis Bacon in the seventeenth. Astronomy contributed the idea of the regular orbital motion of particles from the labors of Ptolemy in the first century down through those of Copernicus and Kepler. The theory of the attraction exerted between masses of matter, as outlined in the work of Galileo, and reaffirmed by Newton, changed alchemy into a science resembling modern physical chemistry. Prior to his execution in 1794, Lavoisier clarified the conception of combustion, discarding the then current idea of phlogiston and making all chemical change answerable to verification by the balance. Then and then only could chemistry be considered a quantitative study.

In the roster of great chemists such names as Roger Bacon, van Helmont, Albertus Magnus, Paracelsus, Boyle, Stahl, Scheele, Priestley, Cavendish, Black and Lavoisier demonstrate the slow but sure development of chemistry until the beginning of the nineteenth century. Thereafter we are indebted to a vast array of patient, earnest workers—Dalton, Davy, Faraday, Dumas, Berthelot, Berzelius, Charles, Gay-Lussac, Morley, van der Waals, Arrhenius, Mendelejeff and many others down to the present day with its almost unbelievable accomplishments in every branch of this rapidly expanding science.

10 Summary

Chemistry had its origin in metallurgy and was long associated with the processing of metals.

As an art it flourished in ancient Egypt, and its devotees brought it to Spain after the fall of Alexandria; thereafter it was known as alchemy.

The ideals of alchemy were not attained, and chemistry became associated with the practice of pharmacy.

Greek thought and medieval mathematics and physics had their influence on chemistry so that from the time of Robert Boyle the investigation of matter was of prime importance.

The skill of Lavoisier aided in interpreting the findings of his predecessors and contemporaries and in placing them on a quantitative basis. Thereafter chemistry emerged as a science.

Questions

1. To what extent do you consider the arts and sciences to have been developed by human necessity?
2. Outline the means by which the chemical art came to southern Europe.
3. Do you think that the aims of the alchemists were different in essence from those of the scientists of today?
4. Chemistry was once held to be a form of witchcraft. Can you recall any story of how witchcraft was punished in the Middle Ages?
5. To what would you ascribe the persecution of witches in North America in Colonial days?

2

The Chemist's Stock in Trade

11 Water

In speculating on the nature of matter the Greek philosopher, who conceived of water as the primal element by means of which all the variations of matter might be explained, chose a substance not merely of universal importance to daily life, but also capable of illustrating the main principles of chemical science. And whereas the oceans, seas, lakes, rivers, rain, dew and clouds because of their great masses may be of prime importance to mariners, engineers, farmers and, indeed, to all other members of the human race (not to mention the lower animals and the plant kingdom), the chemist can discover all the important characteristics of water by the study of a mere cupful of it. Furthermore, a comprehensive knowledge of water will aid in understanding the behavior of other less common but quite important liquids and chemical compounds generally.

Water is called a *liquid*, that is, it requires a container with bottom and sides to prevent its flowing out of reach. On cooling sufficiently, water forms ice. Ice is a *solid*, rigid, and possessing a form which does not flow as water does. Again, with the application of heat, water eventually boils and disappears into the surrounding atmosphere. It is no longer visible since it has become a *gas*, but that it is still present may be shown by letting a cold object stand in the room where the water was boiled away. Moisture will condense on the cold object, and this moisture is water.

12 The Three States

What are ice, water and water vapor? All three are *physical forms* of the same substance—water. Only two of these three

forms are visible to the eye, only two can be felt with the hands, but all three can be weighed; that is, all three forms have mass. In the language of science these three forms illustrate the *three states of matter—solid, liquid* and *gas.* Thus matter can exist in three states and, incidentally, in three only. For the matter just exemplified may perhaps be seen or felt, but in any event it has weight or mass.

13 Mass

From astronomy we have learned the influence of large bodies on each other. Thus two bodies, of whatever they may be com-

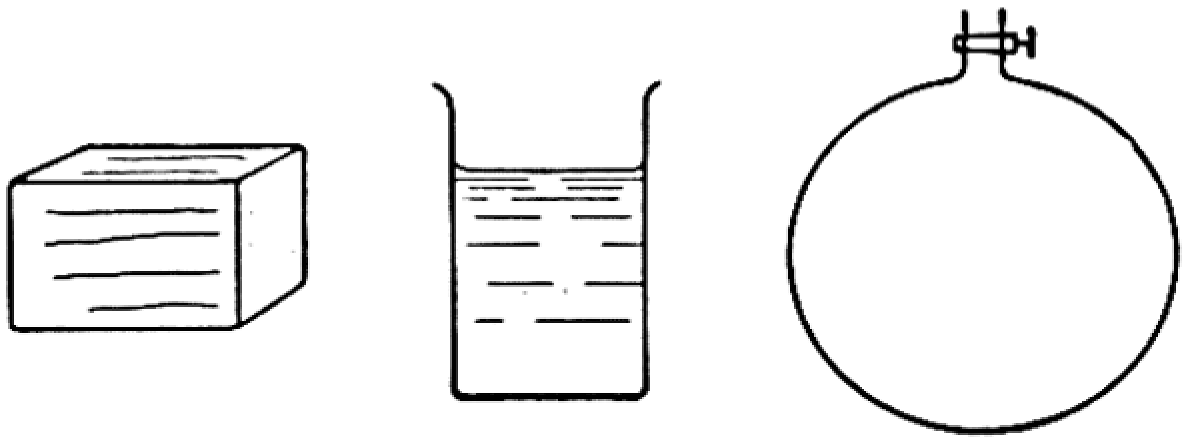


FIG. 1. Matter exists in three forms or states—solid, liquid, gas.

posed, exert a mutual attraction for each other, and this attraction is made up of two factors, the mass of each and their distance apart. This truth is incorporated in a statement (the *law of gravitation*) that *the force of attraction between two bodies is the product of their masses divided by the square of their distance apart.* As far as objects on this earth are concerned, the huge mass of the earth as compared with any large object about us, together with the fairly constant distance away from the earth's center, allows us to consider weight as being relatively invariable. But a pound of something on earth would be much less than a pound on the surface of the moon, which is a much smaller body. Also, the nearer bodies are to each other the more they attract each other. To say, then, that a substance possesses mass implies that it exists. This is matter.

14 Properties

In describing the many materials used in chemistry it is usual to refer to their properties. Thus if ice is a rigid solid, brittle, able to exist as crystals (for example, snowflakes) and able to turn into water, these descriptive remarks are called the properties

of ice. Gold is a soft yellow metal which can be hammered into plates of extreme thinness; such are the properties of gold. And since these properties merely describe the visible characteristics of the substance itself, without telling anything about how gold may be changed so that it can, for instance, be dissolved in water or used for plating on other metals, they are called *physical properties.*

15 Energy and Work

Another term to be introduced here is energy. Energy may be defined as the ability to do work. In the physical sense this ability to do work may be possessed by (1) a body at rest as well as by (2) one actually doing work. For example, a heavy weight suspended a hundred feet above the ground is capable of doing work if once released; thus it can, on falling, crush stones, dig holes, etc. While it is suspended, these capabilities are not being used, although they are present; such a body is said to have *potential* energy. On being released, however, this body will come crashing down, and, because of its height from the ground and also its weight, may be guided to do useful work. When the body reaches the earth and comes to rest, its potential energy has disappeared. In place of this possible work value, the body has the ability to do work due to the weight and motion of the falling body; this kind of energy—that due to a body in motion—is called *kinetic* energy.

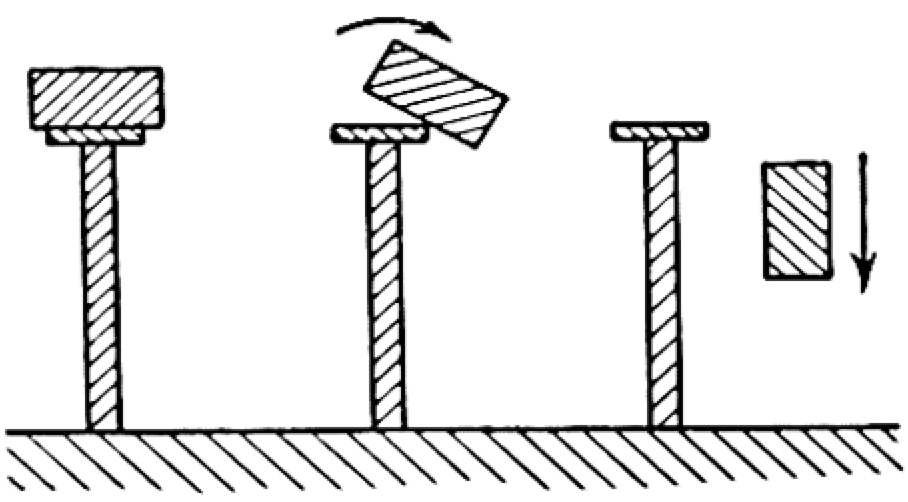


FIG. 2. A body at rest has its potential energy converted into kinetic by falling to the earth.

Energy can manifest itself in a variety of forms, as heat, light, electricity, and in one or the other of these forms it may be added to or taken from a body. Just as the heavy weight referred to above may be raised from the ground to a high position and given potential energy (which is later transformed into kinetic energy to balance that spent in the raising process) for the purpose of doing some mechanical work, so heat or electrical energy may be added to a body, thereby increasing its potential energy. It is not necessary that the form in which energy is added to a body should be the form in which it is later released. Thus mechanical energy (a flow of water down an incline) may give rise to electrical energy

(by means of a dynamo), which in turn may appear as heat or light.

When we add heat to ice, it changes to liquid water, which can flow and so do work. When we add sufficient heat to water it boils off into its vapor (steam), which can be harnessed to do much work. Thus water vapor can be made to do more work than water, and water to do more work than ice. This example shows (1) that a change of state involves heat, (2) that heat can be absorbed and (3) that, of the three states of matter, the gaseous is most active and free.

16 Chemical Substances

As shown above, water may exist in three states. But what kind of matter is water? If water occurring in nature, such as in the sea, lakes, rivers, and descending from clouds as rain or snow, is carefully examined it will be found to contain other matter, such as salt and dust, and is therefore not pure. It may be purified by distillation, that is, by heating it to convert it into the vapor and then by cooling the vapor. This pure water contains nothing foreign to it; it is uniform. Such a uniform material is called a *substance.*

Gold is another substance. A gold coin, however, is not a single substance, for it is a mixture of gold with copper—a mixture of two substances. Similarly, bronze is a mixture of two substances, the reddish metal copper and the silver-white metal tin. Such mixtures of substances are usually called *bodies.* Quantities of matter, whatever their nature, are called bodies, but only perfectly uniform bodies are called substances. All substances are bodies, but not all bodies are substances.

17 Energy Is Put to Work

What has been said so far in this chapter, besides defining terms, has really concerned *physics.* Here, however, is an experiment that is *chemical.*

Connect three or more dry batteries by copper wires to two pieces of metal (Fig. 3) and dip the metal into water which has had a little of a substance called an acid added to it. Immediately bubbles of gas will be seen to come out of the water away from each piece of metal. Some of this gas can be obtained by inverting a test tube, filled with water, just under the surface of the water

and near one piece of metal. The bubbles will enter the test tube and fill it by driving the water out, that is, by displacing the water downward. A lighted match put to the mouth of this test tube will cause a slight explosion. A similar collection of gas from the other piece of metal shows the test tube to contain something which will not burn or explode, but will cause a glowing splinter to ignite.

This phenomenon is explained in this way. The electric current from the batteries (electrical energy) on flowing through the water changes it into two invisible substances, not solid, not liquid, but

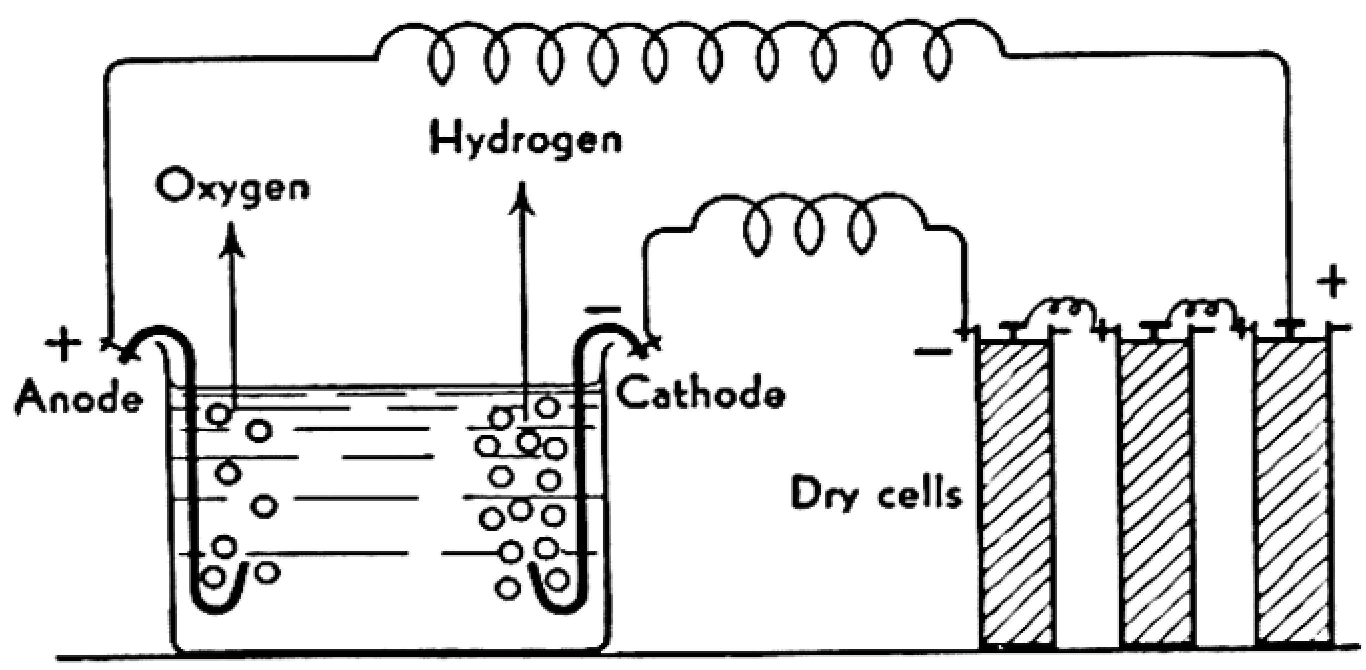


Fig. 3. A direct current of electricity decomposes water into oxygen and hydrogen.

gaseous. These gases are two different substances: the gas which burns is hydrogen; the other gas is oxygen. This formation of two different gases from a single substance is an example of a *chemical change.*

18 Two Simple Elements

So by means of electrical energy water has been changed into two new substances—two different gases. But try as we may, we can find no way to change either hydrogen or oxygen by chemical means into two other simpler substances. Again, if these two gases are mixed and an electric spark passed inside the mixture, an explosion results. Water is formed again, and a great deal of heat is given out. The only conclusion that can be formulated is that water, in spite of its apparently simple nature, is made up of two different substances—the gases hydrogen and oxygen. It is not a mixture of these gases, but a mixture of these gases will give back the water from which they were obtained if the conditions are made favorable for it to do so. Hydrogen and oxygen are therefore *elements.*

19 Some Chemical Epithets

This is a very real and important experiment, for a great deal may be learned from it. When water is thus changed into these two gases which compose it, the operation is called *decomposition* (= the splitting apart of the constituents). When electricity is used to carry out this decomposition, we call it *electrolysis*. When oxygen and hydrogen are made to change back into water, the process is called *synthesis* (= building up). Since hydrogen and oxygen are very simple substances, they are called elements. If these two substances unite to form water, then water in its make-up must be less simple or, in other words, complex. And the complex result of such a union is called a *chemical compound*. The acts of decomposing water and of synthesizing the water again from its elements are examples of chemical reactions.

These simple statements summarize the matter. (1) Water may be decomposed into hydrogen and oxygen by the addition of energy. (2) Hydrogen and oxygen unite to form water with the liberation of energy. (3) A simple mixture of hydrogen and oxygen is not water. These statements illustrate the differences between elements and compounds, and between chemical compounds and mixtures.

20 Energy Takes Its Place

But special mention should be made of the electrical energy put into the water to obtain these gases, or of the heat given off when these gases reunite to form water. All these important points can be brought together in still simpler statements, using an arrow instead of the words *decompose into* and *unite to form:*

$$\text{(1) Water + energy} \rightarrow \text{hydrogen + oxygen}$$

$$\text{(2) Hydrogen + oxygen} \rightarrow \text{water + energy}$$

Actually these two statements can be put together using arrows both ways:

$$\text{Water + energy} \rightleftharpoons \text{hydrogen + oxygen}$$

The one word energy includes electricity, heat, light, etc. In a general sense an arrow, as used above, signifies a chemical change of some sort—a *chemical reaction*, as it is called. This term reaction implies that two quantities (at least) are required for a chemical

change. As will appear frequently later, chemical changes differ from physical changes (which involve color, taste, weight, etc.) in that they concern themselves with a change in composition and in properties. Thus it will appear that hydrogen or oxygen is capable of a behavior of which water is incapable.

21 Matter

Matter, then, is ultimately composed of a limited number of elements which, combining, form an exceedingly large number of different substances. These substances, occurring in varying proportions, constitute the complex matter which we find about us.

The chemist has so many ideas to represent simply that he inclines toward brief, concise statements and representations. A little later the reader will be introduced to the chemist's shorthand system, but not before he has come to understand his longhand. In the meantime, we have the bricks (elements) out of which the chemical buildings (compounds) are constructed. These bricks (elements) are of many kinds, just as the compounds will be found to be varied. But the chief point to stress at the moment is that a heap of different bricks tumbled together is not the finished building; neither is a tumbled heap of elements a compound. It is the orderly arrangement of the proper parts which constitutes the structure, whether we talk of houses or of chemical compounds.

22 Review of Definitions

Matter is that which occupies space and possesses mass.

A body is a quantity or limited portion of matter.

A substance is a body of uniform composition throughout, a pure chemical individual.

A mechanical mixture is an intermingled portion of matter, made by mechanical means, in which the constituent parts are frequently discernible, and from which they may be separated by purely mechanical means.

An element is a simple substance which has not yet been separated by chemical means into two or more simpler substances.

A compound is the result of the intimate union of two or more elements where energy is involved.

Decomposition is the chemical separation of a compound into its constituents, either partially or completely.

Synthesis is the chemical union of simpler substances to form a more complex one.

Energy may be defined as the capacity for doing work. It may be measured in terms of its manifestations—heat, electricity, etc.

A chemical reaction is a change involving two or more substances, producing a change in their properties and involving a transfer of energy in some form.

A law in science is a concise statement of facts supported by incontrovertible evidence. Such a law is not made by man; it is discovered by man.

23 Summary

Three states are recognized in which matter may exist: solid, liquid and gaseous. When matter changes from one state to another this change is accompanied by alteration in physical properties. Water is a good example of matter because it is very common and the three states in which it can exist are well known. Water, the freely flowing liquid, may be frozen into the rigid solid called ice, and may be boiled away to form the gas called water vapor, but more generally known as steam.

But to change water to steam, heat has to be added. Heat is a form of energy. Work has to be done on the liquid water to change it into the gaseous state; heat does this work.

Similarly, heat must be added to a quantity of ice (solid water) in order to change it to liquid water. But though heat is added, no change in weight occurs—only change in form and other physical properties.

Energy may also be utilized to break apart the two different constituents of water. This time electricity is the form of energy that is used. Water, when subjected to electrical treatment, is split up into two different substances—both gases and called hydrogen and oxygen—which have properties different from those of water. These two gases are so simple that they in turn may not be split apart to give rise to simpler entities. They are called elements and, since they together make up water, water is called a compound.

The act of splitting apart these two elements, which together form water, is called a chemical reaction; this type of reaction is known as decomposition.

All changes in physical state involve energy, either going in or coming out. All changes in chemical make-up (composition) similarly involve energy, either going in or coming out.

Questions

1. Illustrate the three states of matter by reference to water.
2. How would you differentiate between matter and energy?
3. Name all the properties you know to be possessed by a piece of ice, a bar of iron, a bar of lead, a sheet of aluminum, a glass of water and a jet of steam.
4. If you wished to find the weight of a pound of butter, first on earth and then on the moon, which would you prefer to use—a balance scale and a pound weight or a spring scale? Why?
5. Why can a certain weight of steam do more work than the same weight of water or of ice?
6. If electricity must be added to a quantity of water to change it to hydrogen and oxygen, should the hydrogen and oxygen together be more energetic substances than water?

3

The Three States of Matter

24 Accuracy of Description

In the previous chapter we have touched upon energy and matter as they may be demonstrated by the well-known substance water. It now becomes necessary to extend this introduction to the whole field of matter. In youth we formed the habit of attempting to describe objects and scenes exactly as our eyes saw them, but without bothering to suggest how they might appear under very different circumstances. Thus we have learned three separate names by which to identify the chemical compound water. These names, however, actually refer to the conditions under which water may exist, so that by using one of the three words—ice, water, steam—we automatically draw attention to these conditions rather than to the chemical substance itself. In this book we shall meet such a variety of substances which have only one name for all conditions of existence that we must keep in the back of our minds this possibility of a threefold existence, unless the conditions are designated. When they are not mentioned it is implied that the conditions are those under which we ourselves exist, that is, normal conditions.

25 Solids

Since most of the materials we know in life are in the solid state—a chair, a glove, a knife—most of our ideas are conditioned by such contacts. By contrast we know very few liquids and still fewer gases. The history of man shows that astronomers speculated on and calculated the revolution of the moon around the earth centuries before Boyle did his classical experiments on that mixture of gases known as air.

If we think of the many kinds of solids which we know we shall find that their physical properties differ tremendously, as the following examples show. If we grasp with the hand a piece of hot iron we may find it highly uncomfortable, whereas a piece of wood or wool, although at the same temperature, does not burn us. Iron, therefore, conducts its heat to our hand more rapidly than the wood and wool. An iron paperweight will be found to be more satisfactory for the purpose than an aluminum paperweight of the same size; it is heavier, volume for volume. A piece of marble may be used in the construction of a building, but not a piece of chalk; the marble is more durable. A piece of beeswax is no harder than a lump of camphor, but the camphor has an odor and will slowly disappear if left outside in the air.

These examples show what a large number of physical properties is displayed by a variety of solids chosen more or less at random. If we confine our attention to those solids which are elements, we can discover certain properties which are shared in common to different degrees or show great contrasts. Copper is harder than gold, but much lighter volume for volume; a scrap of diamond is much harder than either though relatively much lighter; gold and copper will conduct heat and the electric current, whereas the diamond is extraordinarily bad at conducting either. Gold may be hammered into very thin sheets or drawn out into a fine wire with great ease, whereas the diamond will break under such stresses; it is too brittle. Thus we can discover such properties in the elementary solids as relative weight (specific gravity, really), hardness and brittleness (and its reverse malleability and ductility).

26 Solid to Liquid to Gas

But some physical properties are shared by all solids to differing degrees. One of them is the change that takes place on heating, that is, on adding energy in the form of heat. A piece of tin, a soft white metal, on being heated gets hotter until at 232°C it melts and turns into a liquid; it remains a liquid until, at about 1600°C, it again changes its state and becomes a gas, boiling away like water boiling in the open air. If this tin vapor is allowed to pass into a cooler container it will again turn into a liquid and finally (below 232°C) into the solid as we first knew it. Thus a solid has been converted into a liquid, then into a gas, and back again through the liquid into the solid. The heat which was added to

the solid tin imparted energy to the tiny particles of which the block of tin was made up so that their mutual attraction or cohesion was overcome and produced the freely flowing liquid tin.

Further heating overcame the attraction of the liquid particles so that the freer gas particles could separate from one another in the freest of all three states, the gaseous. Removal of heat (by cooling) merely reversed this freedom of movement and allowed the natural cohesion of the tin particles to come into play. Thus the three states of matter are convertible, as we said previously of water, something we knew from early childhood without, perhaps, ever having speculated on "How?" or "Why?"

If the previous experiment had been performed somewhat more accurately, we should have observed that, on first heating the block of tin, it increased in size (that is, in volume) and that this increase continued fairly regularly up through the liquid state until it reached the point in temperature where it became a gas. At this point it would develop a huge volume, just as a small volume of water develops, on boiling, a volume of gas (water vapor) which is over a thousand times that of the liquid itself. Most solids on changing to the liquid state take on a sudden increase in volume of about 5 per cent.

27 Matter and Heat

When any substance in any state has its temperature changed, a definite quantity of heat is concerned with this change. The thermometer is an instrument designed to measure the *degree of heat* of any body whatever it may be and whatever mass or volume it may have. The thermometer usually employed in scientific observations is of the Celsius or centigrade type. On this instrument the freezing points and the boiling point of water are shown as 0°C and 100°C, respectively. These figures correspond exactly to 32°F and 212°F on the Fahrenheit thermometer, which is in general use in households.

The *quantity of heat* concerned with any change in temperature must take into account (1) the kind of body, (2) the mass of that body and (3) the amount of temperature change. The unit of quantity of heat employed in such an instance is the *calorie*. It is defined as the quantity of heat required to raise the temperature of exactly 1 gram of pure water from 15° to 16° on the centigrade

scale mentioned above. These considerations should be emphasized here.

(1) Two masses of the same substance (tin or water or gasoline) will contain the *same quantity* of heat if they are of the same mass and if they show the same *degree* of *heat* (that is, temperature on a thermometer).
(2) Two unequal masses of the same substance may contain the *same quantity* of heat only if they are at certain different temperatures.
(3) Two equal masses of different substances need *not* contain the same quantity of heat since different substances have different capacities for absorbing heat.

28 Water and Heat

When 1 gram of water undergoes a heat change from 15° to 16°C and 1 calorie of heat is *absorbed*, that same amount of heat is *given off* when this gram changes back again from 16° to 15°C. Furthermore, since water (liquid) is used as the standard for heat measurement, this 1 calorie for 1°C change in temperature is called the *specific heat* of water. For water (liquid) from 0° to 100°C this specific heat averages 1 calorie for each change of 1° at a time. Thus 100 calories of heat must be given to 1 gram of water at 0°C to raise it to 100°C.

By comparison, only 0.4 calorie is required to change 1 gram of ice (solid water) for each 1 degree rise in temperature from −20°C to 0°C. The specific heat of ice is therefore 0.4 calorie. Turning finally to gaseous water (water vapor or steam), we find that, at a constant pressure, each 1 gram of water vapor requires 0.465 calorie for each 1 degree change above 100°C.

Water is noted for its high specific heat, that of tin being 0.0559, lead 0.0310 and copper 0.0936. According to the definition of specific heat, it is obvious that it takes a greater quantity of heat to raise the temperature of a mass of water than the same mass of tin, lead, or copper.

Of all substances which we have to study, water is by far the most important and in some respects the most unusual. A gram of ice at 0°C (still solid) has a volume of 1.090 ml. On being changed by heating from solid to liquid water and still at 0°C the volume becomes 1.0001 ml. This temperature (0°C) is the transi-

tion point from solid to liquid. Further heating changes the volume regularly to 4°C, where it becomes 1.0000 ml. This point is known as that of the maximum density of water. If we continue to heat this water it rises slowly in temperature to 100°C (under standard barometric pressure conditions) as its volume increases to 1.043 ml. Continued heating changes the water over into water vapor still at 100°C (the boiling point) until all the liquid has turned into vapor. This 100°C is the transition point from liquid to gaseous water. When all the liquid has become vapor

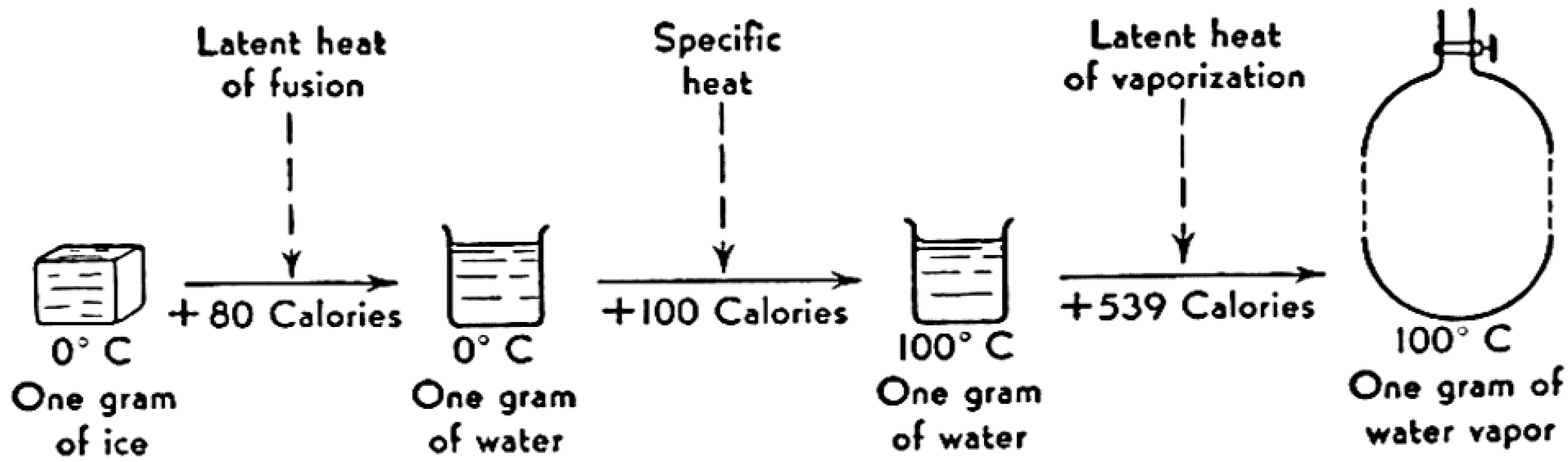


FIG. 4. One gram of ice at the freezing point (0°C) requires about 719 calories of heat to change it to water vapor at the boiling point (100°C), but only 100 of these calories show on a thermometer.

its volume is 1698.8 ml. This startling change in volume from 1.043 ml to 1698.8 ml is characteristic of the transition from the liquid to the gaseous state and, in the case of water, is put to use in the generation of steam power, which has been of such great industrial significance for the past century and a half.

During the course of heating water as shown above, these energy changes occur. From −20° to 0°C heat is absorbed at the rate of 0.4 calorie per gram, the specific heat of ice. During the transition from ice to water, 80 calories of heat per gram are absorbed just to effect this change in state without change in temperature. This quantity is called the *latent heat of fusion* of ice "latent," because it does not show on the thermometer used to follow the change in temperature. Between 0° and 100°C, 1 calorie per gram (specific heat of water) is absorbed for each rise of 1° in temperature. At 100°C, where the transition from water to water vapor takes place at constant temperature, 539 calories per gram are absorbed just to effect this change in state. This quantity of heat is called the *latent heat of vaporization*. When the water has changed into vapor, the vapor (now a gas) continues to rise in

temperature as long as heat is applied and absorbs the specific heat of water vapor (0.465 calorie per gram per degree rise in temperature).

When water vapor is cooled, the reverse of this process takes place. The absorption of specific and latent heats becomes the evolution of heat; meanwhile the increase in volume becomes a decrease and vice versa. Figure 5 illustrates the volume changes during the heating (and cooling) described above.

From the foregoing we have learned that: (1) The various states of matter are interconvertible by means of heat interchange. (2)

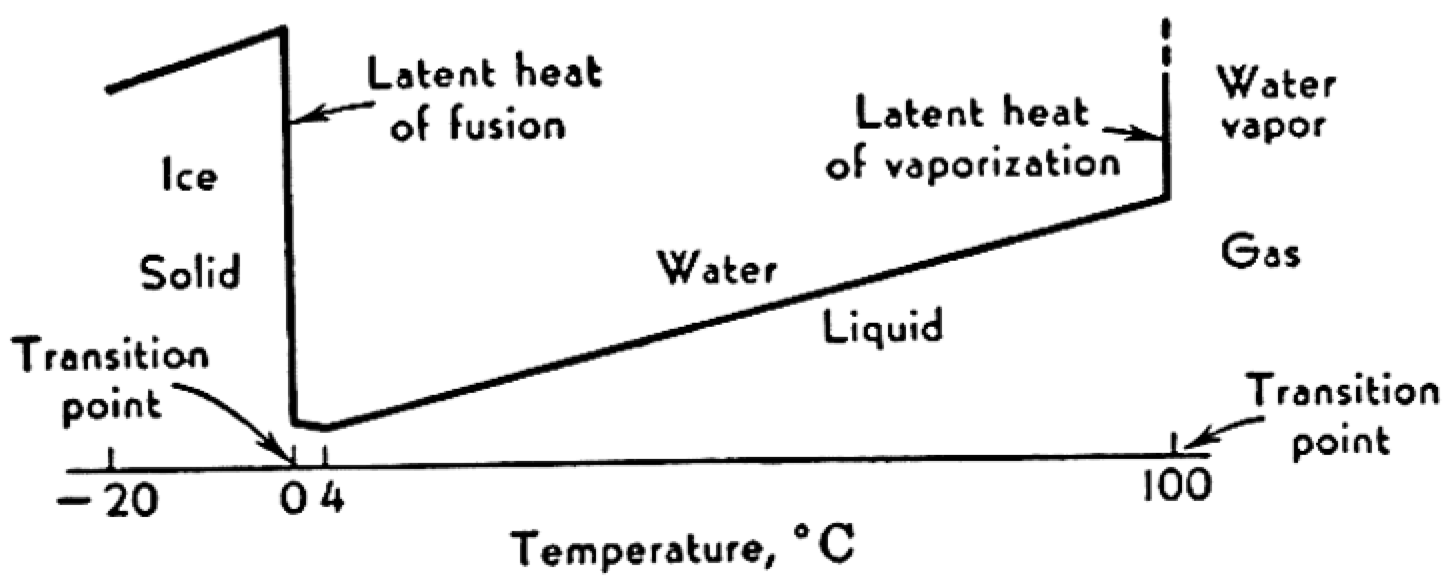


FIG. 5. Volume changes of water with temperature changes.

Change of state, or transition from one state to the next, is always accompanied by a change in heat content—latent heat. (3) Change of temperature of any one state is always accompanied by change of heat content. (4) Heat energy is closely linked with material existence. (5) Volume changes accompany energy changes. The more striking the volume change, the greater the energy change (as at the transition points).

29 Density

When a body of fixed mass increases in volume, its internal texture becomes less compact, that is to say, its *density* decreases. Conversely, when the volume decreases, the density increases proportionately. Density is thus taken as the reciprocal of volume:

$$D = \frac{1}{V} \quad \text{or} \quad V = \frac{1}{D}$$

The word density, as used in practice, means the relative weight of a unit mass of matter compared with an appropriate standard. The density of a gas is found by weighing a known volume of that

gas and comparing it with the weight of a similar volume of air, or hydrogen, or oxygen under the same conditions of temperature and pressure. These conditions, 0°C and 760 mm of mercury pressure, are conveniently referred to as S.T.P. (standard temperature and pressure) or N.T.P. (normal temperature and pressure). Figure 6 illustrates a method of determining the density of gases.

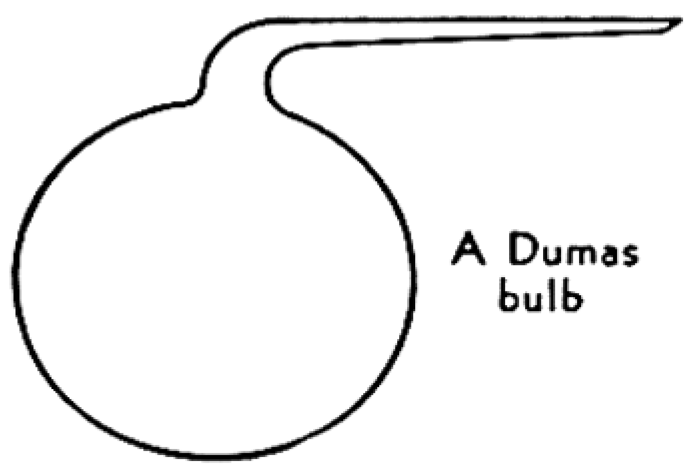


FIG. 6. A simple way to determine the density of a gas is to weigh it. If this volume is weighed for each gas put into it, the ratio to hydrogen (or oxygen or air) is the density. There are more elaborate methods if required.

30 Specific Gravity

The density of liquids and solids is always referred to numerically by comparison with water. Since the weight of a cube of 1 cm side filled with water at 4°C was arbitrarily taken as 1 gram, we can of course find the density of any liquid by weighing 1 gram of it at 4°C. In practice, however, we weigh a known volume of a liquid and state its relationship to the same volume of water at the same temperature (or at 4°C). This gives us a value known as *specific gravity*. Thus

$$\frac{\text{Weight of the body}}{\text{Weight of same volume of water}} = \text{Specific gravity}$$

The specific gravity of a solid is found in a somewhat similar manner.

31 Abnormal Properties of Water

We have dealt at length with water because of its great importance in both scientific and industrial operations. But there are certain features about the behavior of water which are not typical. (1) Water is one of the very few substances which expand on changing from liquid to solid. (2) Water is the only known liquid substance whose point of maximum density is not at the freezing point. (3) Water (liquid) has a very high specific heat compared with other substances. (4) The latent heat of fusion of ice is very high, aluminum approaching it at 77 calories per gram. (5) The latent heat of vaporization is very high, that of ethyl alcohol being only 206 calories per gram.

These five abnormalities are of tremendous importance in nature since they control such phenomena as the surface freezing of water, atmospheric conditions near large bodies of water, refrigeration, and power development. In fact, our environment is largely conditioned by these properties and their exceptional numerical values.

32 Fluidity

When water at 0°C is heated slowly toward 100°C, it undergoes another change. This change can be shown by letting a volume of water, say 10 ml, flow down a tube with a narrow nozzle at the bottom and noting the time of flow on a stop watch. It will be found that water at 0°C will take a longer time than at 10°C and that the warmer the water the faster it will flow. In other words, the *fluidity* of the liquid will increase with the temperature. At 100°C the liquid will change to gas, and it is well known that any gas (for example, air) will flow much more quickly through a pipe than will a liquid; also the hotter the gas the faster it will flow. (See Fig. 7.)

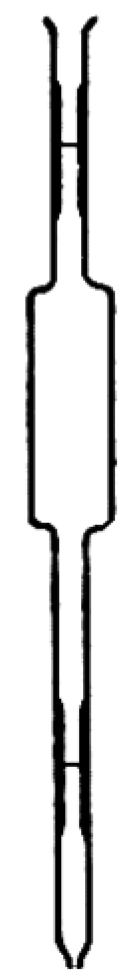


FIG. 7. The fluidity of a liquid can be gauged by timing the flow of a volume at some temperature.

33 Viscosity

The term *fluidity* has been used in the above explanation. A commoner term, however, is *viscosity*, which is used in the inverse sense. For example, a liquid which has a high fluidity, such as gasoline or water, is referred to as having a low viscosity. On the other hand, glycerin, which flows slowly, that is, has a low fluidity, is described as viscous or possessing a high viscosity. This property of viscosity is of considerable importance in the paint and motor oil industries. The behavior of machinery is closely related to the viscosity of the lubricating oil, whose value, in turn, is largely determined by the change in viscosity brought about by high or low temperatures.

34 Surface Tension

Another physical property which water may be used to illustrate is *surface tension*. It is a common parlor trick to attempt to float a steel needle on the surface of water in a tumbler, and as

long as the needle is not immersed in the water this feat is practicable. When the needle sinks beneath the surface, however, its weight relative to water causes it to fall to the bottom. Evidently the conditions existing below the surface of the water are different from those at the surface. This *is* the case, and the difference in conditions can be explained by the attraction of all the particles of water for one another, there being no water particles above the surface. It is apparent that solid water will show this property to a high degree and that water vapor has no such characteristic behavior. (See Fig. 8.)

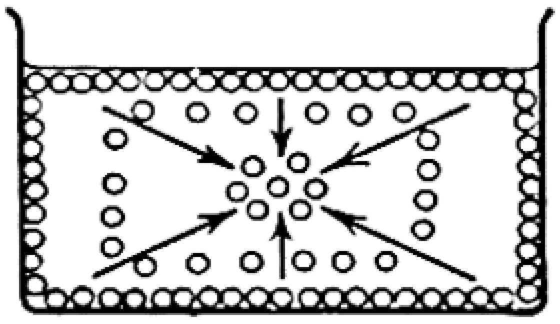


FIG. 8. A needle may be floated on the surface of water because the water particles at the surface are drawn tightly toward the center.

The terms fluidity and viscosity commonly refer to liquids and gases but not so commonly to solids, whose rigidity or resistance to flow is well known. The term surface tension is used only in connection with liquids. But we can think of solids as having fluidity, however small, since glaciers do flow. By contrast, gases would possess a very high fluidity and a very low viscosity. Similarly, if a needle will float on water, it will surely float on a lump of ice and fall rapidly to the bottom of a volume of gas; thus we can say that the solid state of a substance has an infinitely great surface tension and the gaseous state of that substance none at all.

The viscosity of a liquid decreases sharply as the temperature rises until it almost disappears at the transition point to gas. Similarly the surface tension decreases, disappearing completely at the boiling point. If the viscosity is a measure of the friction between molecules, an increase of temperature reduces this internal friction, which should disappear as the gas assumes its large volume at the boiling point. Again, if the surface of a liquid represents the cohesion of its molecules, an increase in temperature reduces this cohesion. Therefore the gaseous state, with its phenomenally large volume in contrast to that of the liquid, is one of great freedom for the molecules; this freedom is gained by the absorption of heat energy. By inference we also conclude that the internal friction and cohesive forces in a solid are very great.

35 The Vapor Pressure of Solids and Liquids

There are two common occurrences which tell us a great deal about liquids and solids. (1) A quantity of pure water exposed to the atmosphere in an open bowl gradually disappears. (2) When a handkerchief is dipped in water and hung outdoors in cold (say, zero) weather, the solid ice that at first encases the handkerchief slowly disappears until the article is completely dry. These two facts tell us that water does not need to be heated to boiling in order to evaporate; indeed it evaporates at all temperatures in-

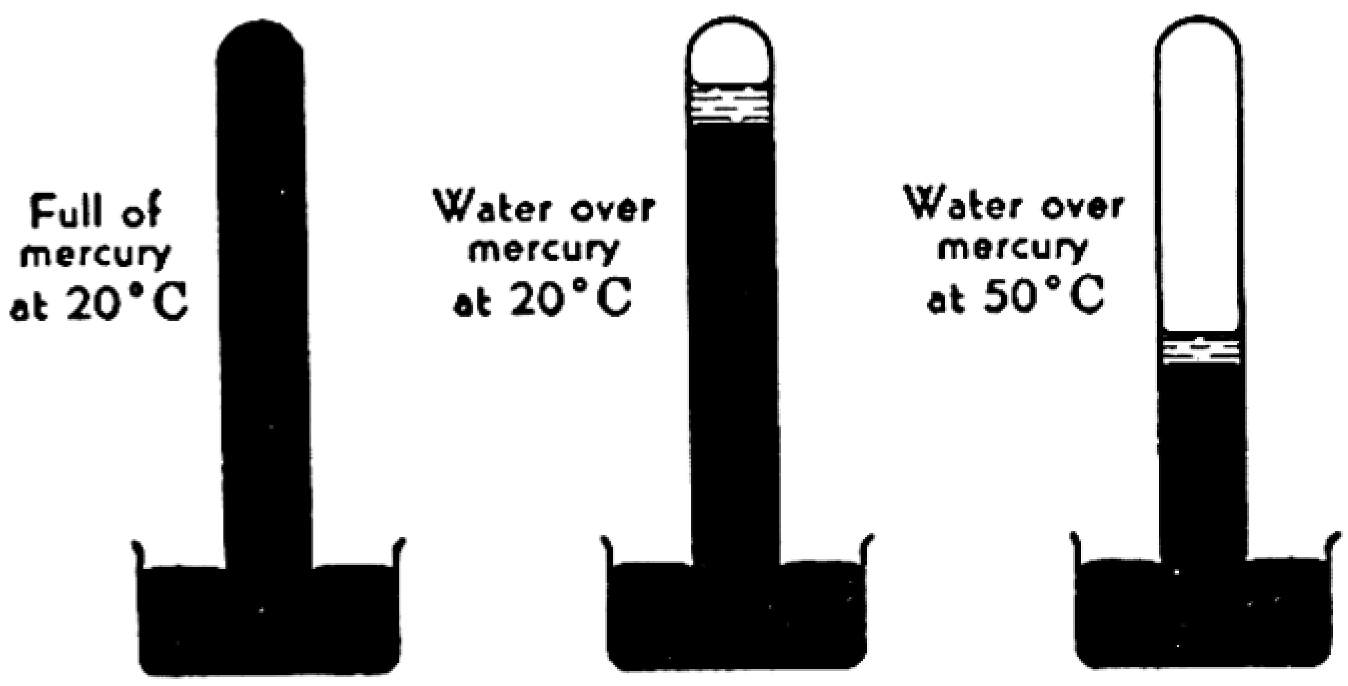


FIG. 9. The vapor pressure of water increases with temperature.

dependently of whether it is liquid or solid. Of course the colder it is, the slower the water (or ice) is in evaporating, and this evaporation cannot go on unless latent heat (of vaporization) is absorbed from the surroundings. Another simple experiment points up the last sentence. If air is bubbled through water, which is at the same temperature as the air to begin with, the water evaporates rapidly but the temperature of the water drops considerably. The explanation of this drop in temperature is that the latent heat of vaporization required to allow the water to evaporate has come from the quantity of heat in the body of the water itself.

It is not difficult to show that water and all other liquids are trying to evaporate all the time, even in an enclosed space. Figure 9 shows an inverted glass tube full of mercury with its open end immersed in more mercury. If a drop of water is inserted (for instance, from a dropper) so that it floats to the top of the mercury in the tube, an open space will appear above the mercury. This open space contains water vapor, and the mercury level in the tube is depressed to a level consistent with the temperature. If the whole apparatus is warmed up a few degrees, the volume of

this open space will increase and the level of the mercury will sink still lower. Further heating produces a similar result just so long as the open space contains some water. These observations can be summed up by saying that the vapor pressure of a liquid increases with increased temperature; the reverse is also true, that the vapor pressure decreases with decreased temperature. If this summing up is correct, hot water should evaporate more quickly than cold water; this is true. Also, if the water molecules have to burst through the surface of the water to get out, it should be easier for the water to evaporate at a high temperature, since the viscosity and surface tension of the water are less, than at a lower temperature. These statements conform to known facts.

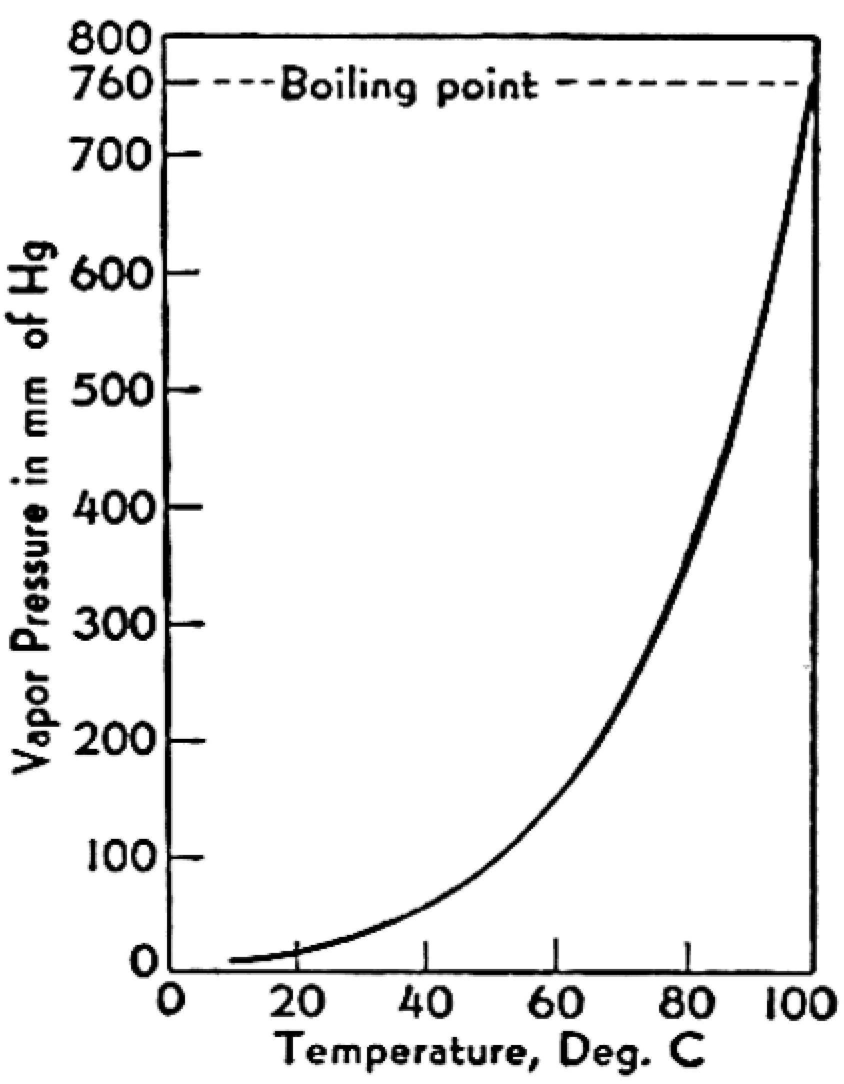


FIG. 10. The vapor pressure of water increases with the increase in temperature

The curve of Fig. 10 shows how the vapor pressure of water behaves with temperature, provided that the external or atmospheric pressure remains the same.

We can therefore picture what must occur in a volume of water open to the atmosphere. A molecule of water picks up enough energy (from heat) to attempt to break through the surface, for the surface contains a great deal of so-called surface energy holding the molecules back. If this molecule gets out, there is the atmospheric pressure (14.7 pounds to the square inch or 760 mm of mercury) to contend with. As long as the temperature of the water remains constant, the surface tension will not change. But if the external (atmospheric) pressure should become less, the chances are much greater for the molecule to get away altogether. (Perhaps a suitable analogy is the escape from a barbed wire enclosure surrounded by guards, where the guards represent external pressure.) The escape of the molecules is therefore dependent upon the external pressure. Hence we can see why such a liquid as water will evaporate much more rapidly when the barometric pressure drops. Now boiling (or *ebullition*, as it is called) is the escape of the molecules through the surface with the same pres-

sure as is exerted upon the liquid by the atmosphere (see Fig. 10). Boiling can therefore occur, in the case of water, for example, at a temperature lower than 100°C if the atmospheric pressure is less than 760 mm of mercury. Pursuing this point further, we can see that, at a high altitude above the earth's surface, the boiling point of water can be very low. Indeed it is known that an egg cannot be cooked by boiling it on the top of a fairly high mountain.

Table 1 is given, as a matter of interest only, to show how the boiling point of water does vary with atmospheric pressure.

TABLE 1

HOW THE BOILING POINT OF WATER VARIES WITH BAROMETRIC PRESSURE

Barometric Pressure, mm mercury	*Boiling Point, degrees centigrade*
680	96.91
710	98.11
740	99.25
760	100.00
780	100.73
800	101.44

This table can be extended, of course, in both directions.

What has been said in the above paragraphs about vapor pressure (sometimes called vapor tension) applies to all liquids, although the degree to which a liquid is affected depends upon the temperature range between its freezing point and its boiling point. It is noteworthy that liquid water has a short range of existence on the temperature scale—0°C to 100°C. By comparison, liquid ethyl alcohol has a range of 196°C, methyl (or wood) alcohol one of 162°C, glycol (so useful in anti-freeze mixtures) one of 209°C, while for glycerin the range is 308°C.

The action of heat on a substance is pictured satisfactorily in this way. A solid at a low temperature consists of small particles in a state of mild agitation or vibration, with a rigid surface and maximal viscosity. As this solid is slowly heated, this agitation increases with the absorption of heat producing the agitation until, with a large absorption of latent heat at the melting point (latent heat of fusion), the rigid surface suddenly breaks down, the viscosity sharply decreases and the liquid state is reached. Continued heating of this liquid further increases the vibration of the

particles, with consequent decrease in viscosity and surface tension until, with a large absorption of heat (latent heat of vaporization), the tenuous surface disappears entirely, and the viscosity almost so, to give rise to the rapidly moving particles characteristic of a gas free to move in all directions at great velocity. Heat thus becomes unalterably linked with the movement of particles of matter, which, in the case of a gas, are called molecules. This is the

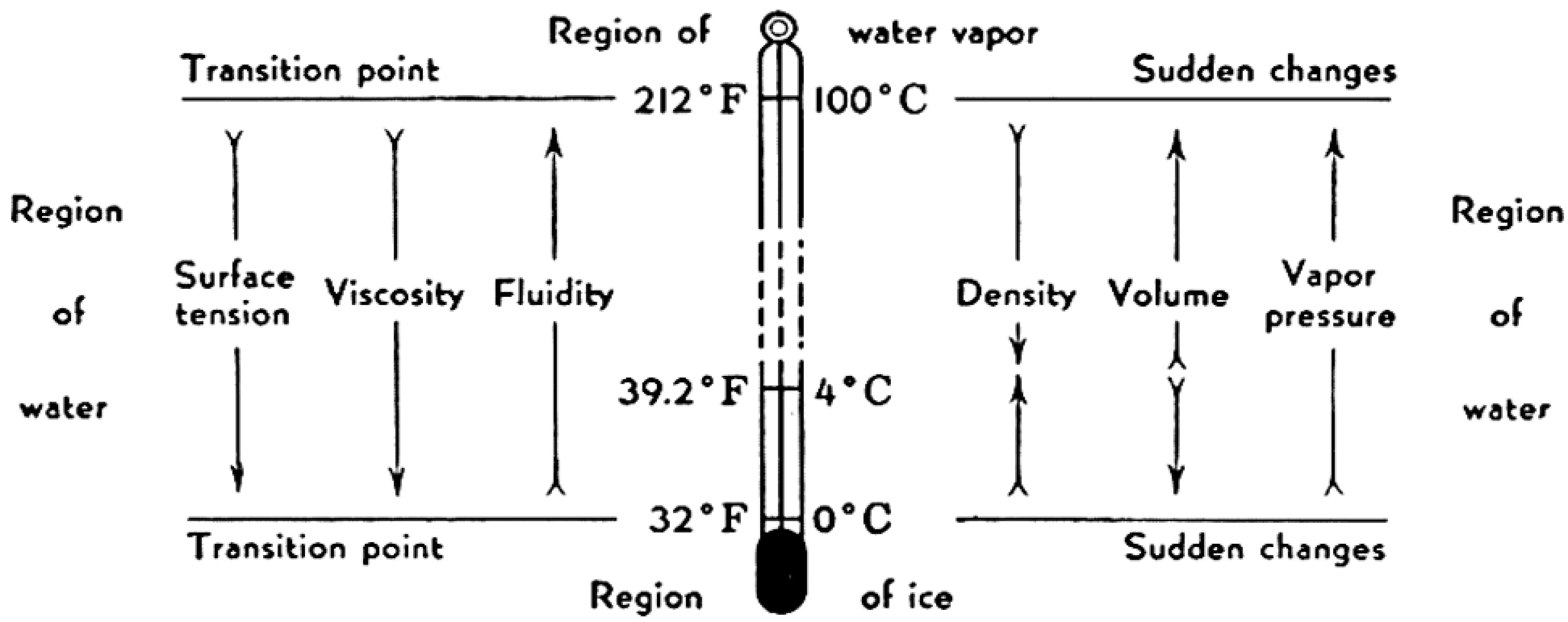


FIG. 11. The physical properties of water change with the temperature. (Direction of arrows shows increase.)

basis in fact of the kinetic theory of matter, treated later in the study of gases.

36 Review of Definitions

The calorie is the unit of quantity of heat. It is that quantity of heat which will raise the temperature of 1 gram of water from 15° to 16° on the centigrade thermometer scale.

The temperature of a body is its degree of heat relative to that of some standard in a fixed condition. It is measured on an arbitrarily devised scale by an instrument known as a thermometer. The type of thermometer most used is the centigrade, where the freezing point of water (a fixed point) is shown as 0°C. Relative to this fixed point, the boiling point of water (another fixed point under proper atmospheric pressure) is 100°C.

The specific heat of a body is the quantity of heat required to raise 1 gram of that body through 1°C.

The latent heat of fusion of a body is that quantity of heat required to change 1 gram of that body from solid to liquid at its melting point. The freezing point of a liquid is the same as the melting point of the same body in the solid state.

The latent heat of vaporization of a body is that quantity of heat required to change 1 gram of that body from the liquid state to the gaseous state at its boiling point. The boiling point of a liquid is the same as the liquefaction point of the same body in the gaseous state.

A transition point is a point on a thermometer scale where a change in state occurs.

The volume of a body is the space that it occupies.

The density of a body is the mass of that body compared with the mass of the same volume of some body taken as the standard.

The specific gravity of a body is the density of that body related to the density of some standard; or the ratio of the weight of any volume of a body to the weight of an equal volume of some standard body, for example, water for solids and liquids. The temperature at which the measurement is made is usually stated since volume always changes with temperature.

The fluidity of a body is the ability of that body to flow relative to a standard. Viscosity is the reciprocal of fluidity.

Surface tension is the property possessed by liquids where the forces of the molecules produce a constricted area at the surface, tending to bring the molecules into the minimum volume possible.

The vapor pressure of a substance (solid or liquid) is the pressure at which that substance is giving off its molecules into its surroundings; it is usually measured in millimeters of mercury and at some stated temperature.

37 Summary

When a solid changes to a liquid it absorbs latent heat—the latent heat of fusion. Latent heat in the change of ice to water is 80 calories per gram at 0°C. When 1 gram of water at 0°C changes back to ice at 0°C, 80 calories of heat are given off.

When a liquid becomes a gas, it absorbs heat; at the standard pressure of 760 mm of mercury, in the change from water to water vapor at 100°C, this heat is 539 calories per gram. On changing back to water, the water vapor gives up the same quantity of heat, a quantity known as latent heat of vaporization.

Most substances expand fairly regularly on being heated from below their melting point to their boiling point. Water is an exception to this rule in that when ice is warmed it expands until it melts. On melting, however, there is a contraction in volume which continues up to 4°C, which is the point of maximum density of liquid water and also the point of minimum volume. From 4°C onwards to 100°C the volume increases, the density decreasing.

All liquids possess fluidity (see viscosity), surface tension and vapor pressure, properties which vary (1) from substance to substance and (2) with temperature. Solids display vapor pressure but not to the same degree as liquids.

Water shows several properties to a degree quite unlike that of most other substances.

The boiling points of liquids vary (1) from liquid to liquid and (2) with pressure.

Questions

1. What changes does water undergo when subjected to heat?
2. Differentiate carefully between latent and specific heats.

3. Define and illustrate the properties fluidity, viscosity, surface tension and density.
4. If a lump of material of the same specific gravity as water were dropped into a body of water, how would it behave?
5. If ice had no latent heat of fusion, how useful would it be as a refrigerant?
6. On very cold nights farmers frequently put tubs of water in the cellars where they store fruits and vegetables. What is the reason for doing this?
7. How much heat has to be withdrawn from 50 grams of steam at 100°C in order to change it to water at 50°C?
8. What sort of world would this be if the maximum density of water were at its freezing point?
9. On freezing, ice forms at the surface of a lake. Why? What temperature would you expect the water at the bottom to have?
10. Why should the filling of a submarine's tanks cause it to sink to the bottom instead of staying anywhere just below the surface?
11. If a fine spray of oil is poured on sea water, why does the oil form in patches rather than remain as isolated droplets?
12. Why is a quantity of water with its surface exposed to the atmosphere usually at a lower temperature than the atmosphere above it?
13. Is the temperature of water higher when it is boiling very rapidly than when it is boiling steadily but slowly? Give the reason for your answer.

4

Chemical Composition—Water and Its Constituents

38 Electrolysis

The simple experiments shown in Fig. 3 can be performed more satisfactorily in the Hofmann apparatus (Fig. 12). This apparatus consists of three vertical tubes joined together at the base so that liquid may pass freely from one to another. One of these tubes has a flanged bulb at the top; the other two end in stopcocks. Near the bottom of each of the two tubes carrying the stopcocks is a piece of platinum foil joined to a piece of platinum wire, which is sealed through the wall of the tube and appears on the outside. If the apparatus is filled almost to the top of the reservoir arm and the platinum wires are connected to a source of direct current electricity, such as a pair of dry cells, bubbles of gas will be seen to rise from the platinum and collect beneath the stopcocks. They displace the water, which consequently rises in the reservoir. In time it will be observed that one tube contains about twice as much gas as the other.

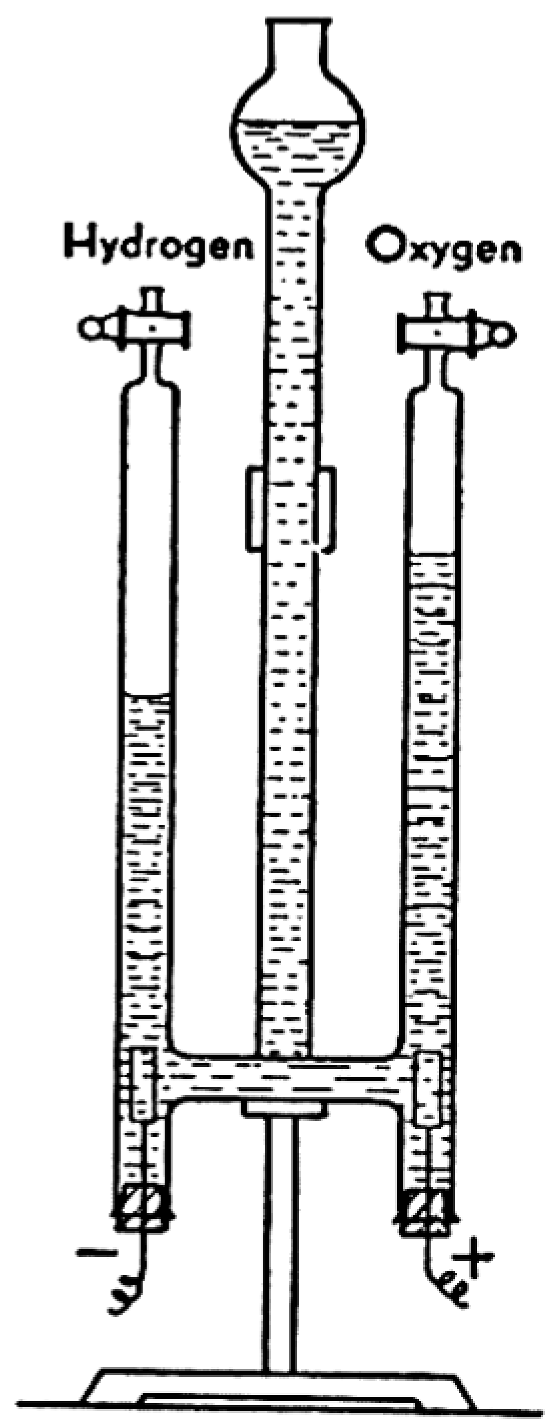


FIG. 12. The electrolysis of water in the Hofmann apparatus gives 2 volumes of hydrogen to 1 volume of oxygen.

On opening the stopcock enclosing the smaller volume, we find that the gas coming out responds to all the tests for oxygen, whereas the other gas will burn in the air if a flame is applied to it. By this method enough of these gases can

be prepared to observe their physical and chemical properties; they are found to lack color, odor and taste.

This decomposition by means of electricity, called *electrolysis*, may be represented thus:

Water + energy → 2 volumes of hydrogen + 1 volume of oxygen

But this is the reverse of what can easily be shown to occur when water is formed from hydrogen and oxygen:

2 volumes of hydrogen + 1 volume of oxygen → water + energy

The decomposition of water is reversible because hydrogen and oxygen can be made to unite to form water and give out energy (this time as heat).

HYDROGEN

39 Chemical Decomposition of Water

(1) *By Metallic Sodium.* A piece of the soft, white metal sodium when dropped into water rapidly decomposes it, giving off a stream of hydrogen gas. When the sodium has disappeared a substance called sodium hydroxide is left dissolved in the remaining water. When freed from the water it is a white solid (soda lye), but when dissolved in water it has the ability to turn red litmus blue. This action is the reverse of what acids do to litmus, and substances that have this action on litmus are called *alkalies.* Coloring matters such as litmus, which change color in the presence of an acid or an alkali, are known as *indicators.*

(2) *By Metallic Calcium.* Calcium, another metal somewhat resembling sodium, has a similar action on water, except that it acts less violently, producing hydrogen more slowly and leaving behind in the water a solution that also turns red litmus blue, known as calcium hydroxide (or common limewater). It has a less caustic taste than sodium hydroxide and is used internally in the human stomach as an antacid, whereas sodium hydroxide solution is very corrosive and should not be allowed in contact with the skin.

(3) *By Metallic Magnesium.* Water may be made to evolve hydrogen if, while boiling, small pieces of the metal magnesium are added to it—a result not discernible in the cold. The residue in this instance is the relatively insoluble magnesium hydroxide, which gives an opalescence to the water.

(4) *By Metallic Iron.* If iron filings are heated in an iron tube to redness and steam is passed over them, hydrogen is liberated and passes off as a gas, leaving behind a dark powder of iron oxide, this is a compound of iron and the oxygen of the water so decomposed.

These experiments show that water may be decomposed by certain metals; most easily by sodium, with less ease by calcium, with more difficulty by magnesium and with most difficulty by iron. This order may be termed the order of decreasing activity of these metals (see page 191).

40 A Laboratory Method

All acids contain hydrogen and may be decomposed by metals to cause the liberation of this hydrogen. When it is necessary to prepare a quantity of hydrogen for experimental purposes, this is the usual procedure. A simple and useful apparatus for this work, known as a Kipp generator, is shown in Fig. 13. A quantity of zinc is placed in the middle bulb and held in place by a suitable screen. Some acid diluted with water is poured in at the top, and, when the stopcock is opened, it comes into contact with the zinc, producing hydrogen gas; this passes out by the stopcock. If the stopcock is then closed, the pressure forces the acid down to the bottom bulb (and of course up into the top bulb) out of contact with the zinc so that no more gas can be formed until the stopcock is again opened.

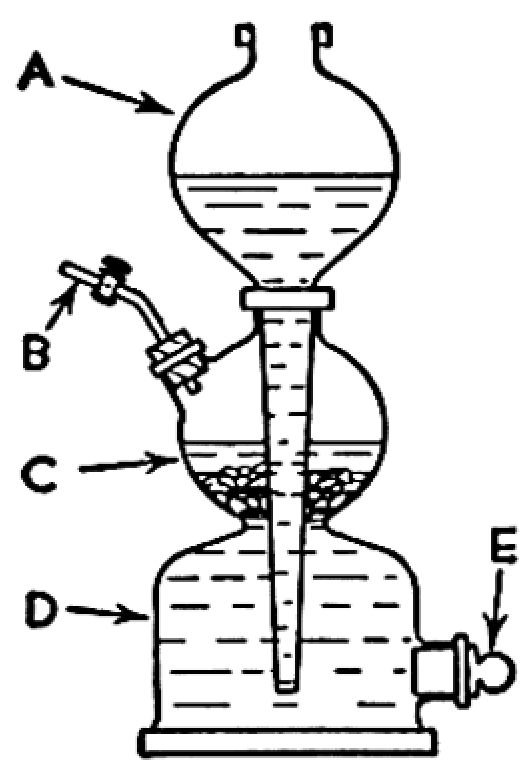


FIG. 13. A Kipp generator for gases. The acid is poured down into *A*, whence it flows into *D* and rises in *C*; *C* contains some solid with which the acid will react to form a volume of gas in *C*. *B* is the gas outlet, and *E* is an outlet for emptying.

41 Physical Properties of Hydrogen

The most important physical property of hydrogen is its lightness compared with other substances. It is best shown in Fig. 14, where a large beaker is suspended upside down on one arm of a balance and is counterweighted. If a jar of hydrogen is opened underneath this beaker, the gas rises rapidly to the top (bottom) of the beaker, displacing the heavier air downwards out of the beaker; this arm of the balance then rises, showing a lesser weight on that side. After a while the balance will resume its normal position, because of the

diffusion of the hydrogen away from the beaker and the return of the air.

This is an important experiment because it shows (1) that hydrogen is much lighter (less dense) than air and (2) that gases can move freely one into another, that is, diffuse.

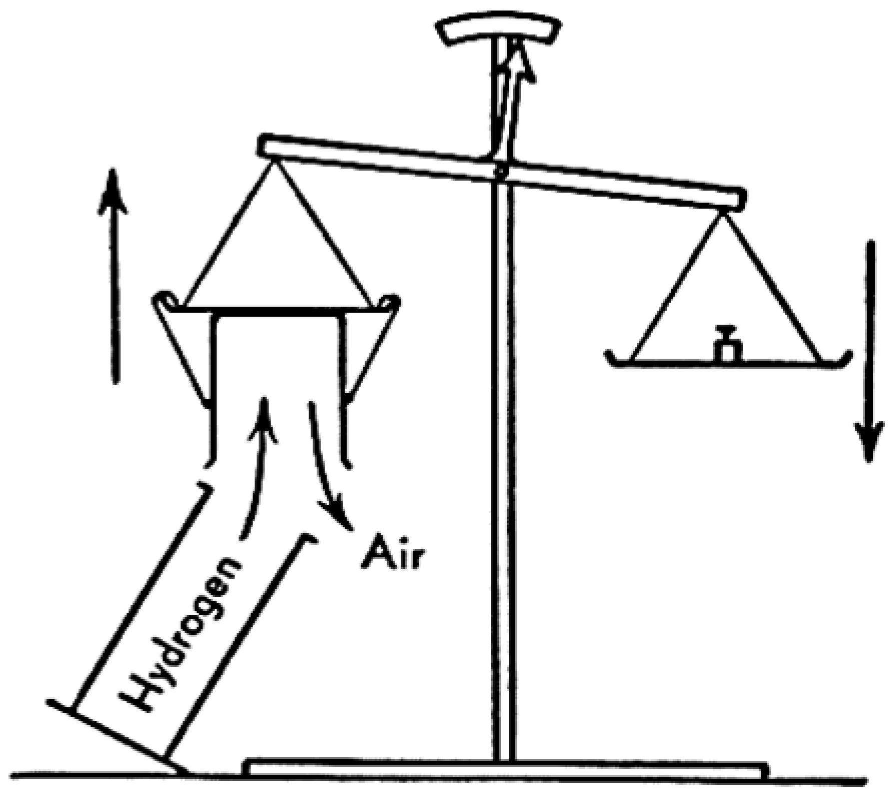


FIG. 14. Hydrogen replaces air and demonstrates its lightness. This is the principle used in operating balloons.

OXYGEN

42 An Important Past

The record of the discovery of oxygen dates back to 1784 and is connected with the names of Priestley, Lavoisier and Scheele. Lavoisier heated a quantity of the liquid metal mercury in the air by converging on its surface the sun's rays, using a magnifying glass for that purpose. This intense heat produced a red powder which was seen to form as a scum on the surface of the mercury. This powder was removed and later heated by itself; whereupon it changed back to mercury, and gave off at the same time an invisible gas which rekindled a glowing splinter of wood.

This was a most important experiment. Mercury had taken a gas from the atmosphere and combined with it to form a new substance. The new substance, on being heated, gave back this gas and the original mercury. Lavoisier called this gas oxygen as he believed it to be a constituent of all acids. In this he was correct at the time. Later, however, acids were discovered containing no oxygen at all, and it became apparent that their essential constituent is hydrogen.

The above method of preparing oxygen is now chiefly of historical interest since it marked a definite turn in the path of chemical progress. Other methods are given briefly below.

43 Preparation of Oxygen

(1) *From Potassium Chlorate.* This substance, a white crystalline solid, on heating gives off oxygen. It may be collected by the

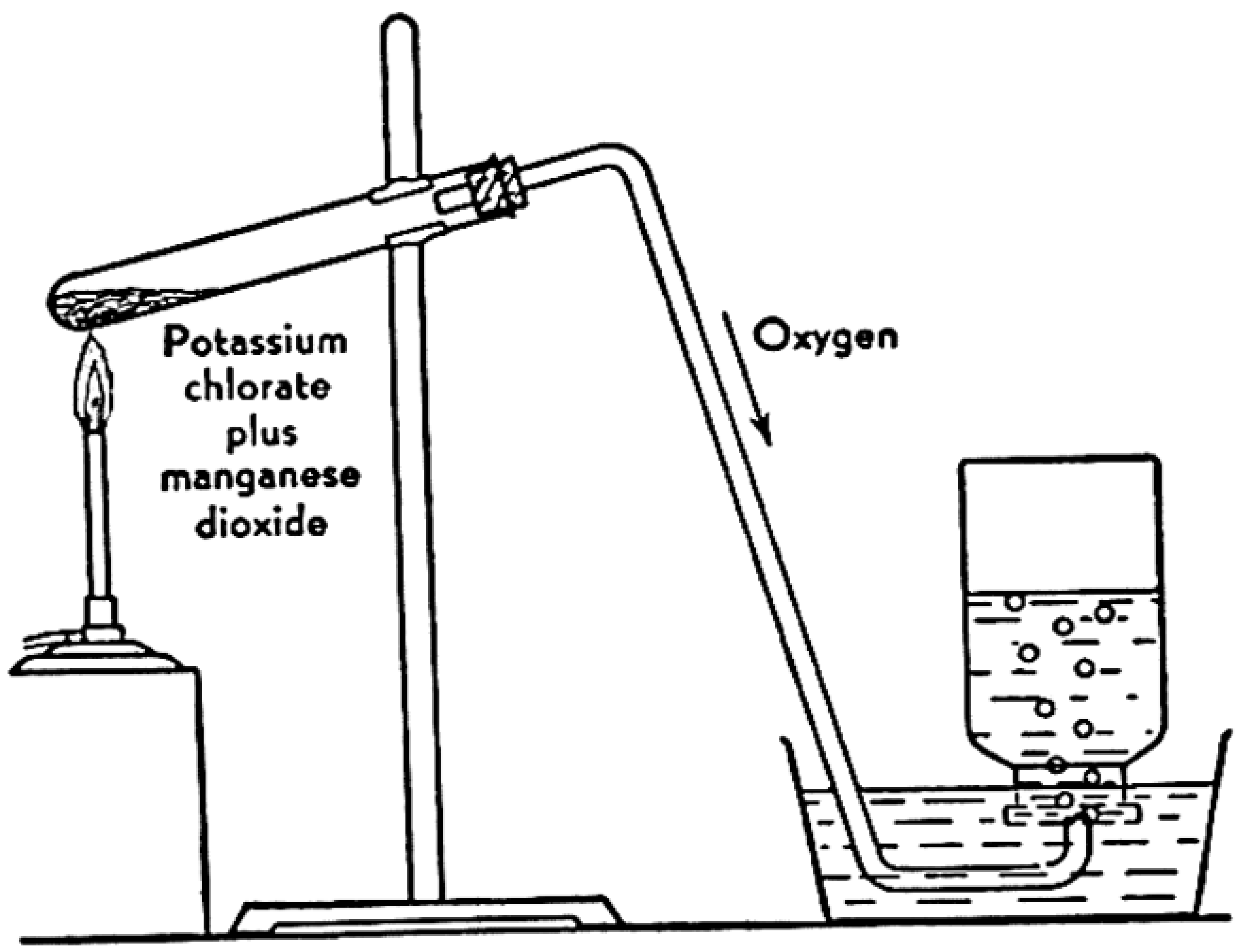


FIG. 15. The laboratory preparation of oxygen from a mixture of manganese dioxide and potassium chlorate, and its collection by means of the pneumatic trough.

method devised by Priestley, known as the pneumatic trough (Fig. 15); a white solid of lesser weight remains behind. This reaction may be summarized so:

$$\text{Potassium chlorate} \rightarrow \text{potassium chloride} + \text{oxygen}$$

If some powdered manganese dioxide is intimately mixed with powdered potassium chlorate before the heating, oxygen will be given off at a lower temperature and with greater efficiency. Afterwards, the manganese dioxide may be recovered unchanged. Any such substance which aids a chemical change without itself being changed is called a *catalyst*.

(2) *From the Air by Liquefaction.* It is possible so to dry and purify the air that practically only oxygen and nitrogen remain. If this mixture of gases is alternately compressed and expanded, it can be cooled down until it becomes liquid. This liquid, if allowed to evaporate slowly, becomes separated into the two gases,

each in a relatively pure state, so that they can be forced into cylinders and kept there for future use.

44 Properties of Oxygen

Examination of a quantity of oxygen in a glass jar reveals it to be colorless, with no odor or taste; indeed very similar to air. It is slightly soluble in water. The chemical properties are best illustrated by trying to burn in oxygen some substances which are known to burn in air:

(1) A glowing splinter of wood, if plunged into a jar of oxygen, bursts into a vigorous flame.
(2) A piece of charcoal, set glowing in a flame, burns rapidly in oxygen.
(3) Sulfur, just glowing in air, will burn brilliantly in this gas.
(4) A small piece of yellow phosphorus (a soft non-metallic element) ignites spontaneously in oxygen, giving rise to dense white fumes.

45 Oxides

If the above tests are made in closed gas jars, it will be found in each of the first three cases that a gas remains after burning has stopped, and that each gas dissolves readily in water. This can

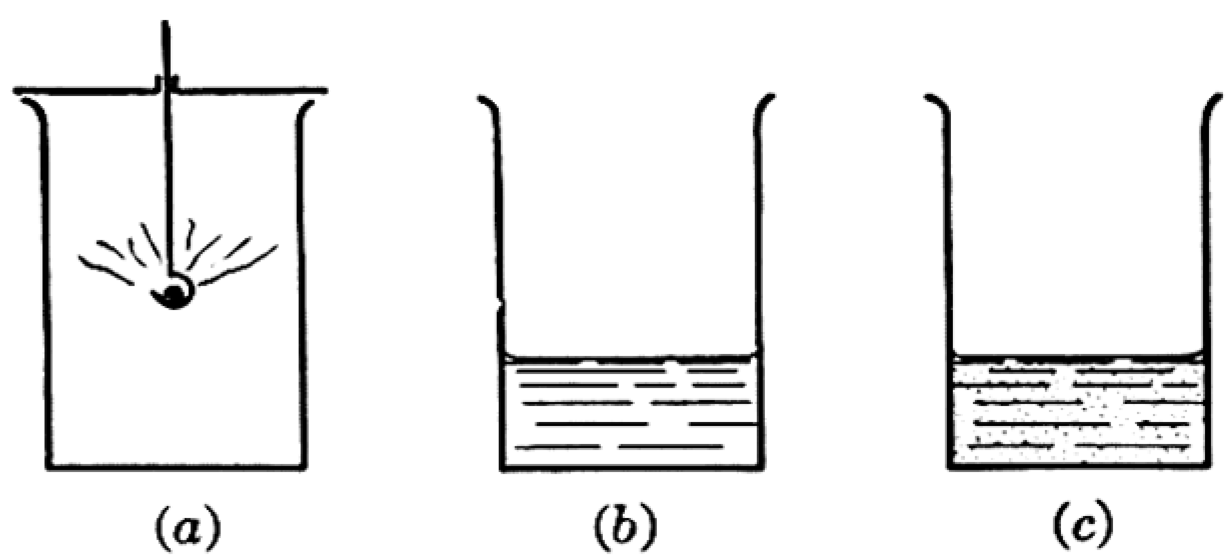


FIG. 16. Sulfur will burn in oxygen to give a colorless gas (*a*); this gas will dissolve in water to form a colorless liquid (*b*). On the addition of litmus (purple), this liquid develops a red color (*c*), indicating the presence of an acid.

be shown by adding water to each jar, shaking it well, and then adding a solution of litmus. Oxygen and water have no effect on litmus, but these gases, dissolved in water, turn litmus from blue to red. Phosphorus and oxygen produce white fumes. These fumes consist of tiny, white particles of an oxide of phosphorus,

which also dissolves in water to turn litmus from blue to red. These gases and fumes are found on analysis to be compounds formed between oxygen on the one hand and these elements on the other.

Wood splinters and charcoal contain large quantities of the element carbon, which burns in oxygen to produce the gas carbon dioxide:

$$\text{Carbon} + \text{oxygen} \rightarrow \text{carbon dioxide}$$

In the same way the reaction between sulfur and oxygen gives the gas sulfur dioxide:

$$\text{Sulfur} + \text{oxygen} \rightarrow \text{sulfur dioxide}$$

The case of phosphorus is a little more complicated, but the same kind of statement may be written:

$$\text{Phosphorus} + \text{oxygen} \rightarrow \text{oxides of phosphorus}$$

The word *oxide* is used with the following significance: it refers to a chemical compound composed of *two elements only*, one of which is *oxygen*.

46 Some Acids

In the tests above, these three non-metals burned vigorously in oxygen to give oxides. Later these oxides were found to dissolve in water, the resulting mixtures (solutions) being found able to turn litmus to a red color. All sour-tasting substances do this, and such substances are called *acids*.

Thus a great deal of chemistry is learned from these simple experiments, which may be summarized thus:

$$\text{Non-metals} + \text{oxygen} \rightarrow \text{oxides of non-metals}$$

and

$$\text{Oxides of non-metals} + \text{water} \rightarrow \text{acids}$$

47 Combustion

In reviewing what occurred in the gas jars where carbon, sulfur and phosphorus were burned, it will appear that what happened there was only a more rapid and vigorous duplicate of what occurs in air itself. Thus carbon and many other substances will burn in the atmosphere simply because the latter contains oxygen; but the burning is less vigorous because the atmosphere is only one-

fifth oxygen. When we realize how much oxygen surrounds the earth's surface, it will be apparent how important this burning is. The more general term for this process of burning is *combustion*, a word derived from the Latin and meaning burning together.

While these three elements are burning in oxygen, so much heat is given out that the gas jars and their contents become quite hot. Also a bright glow is visible at the surface of each non-metal. This process of combustion is the union of two chemical substances (one of which is oxygen) with the production of (1) a new substance, (2)

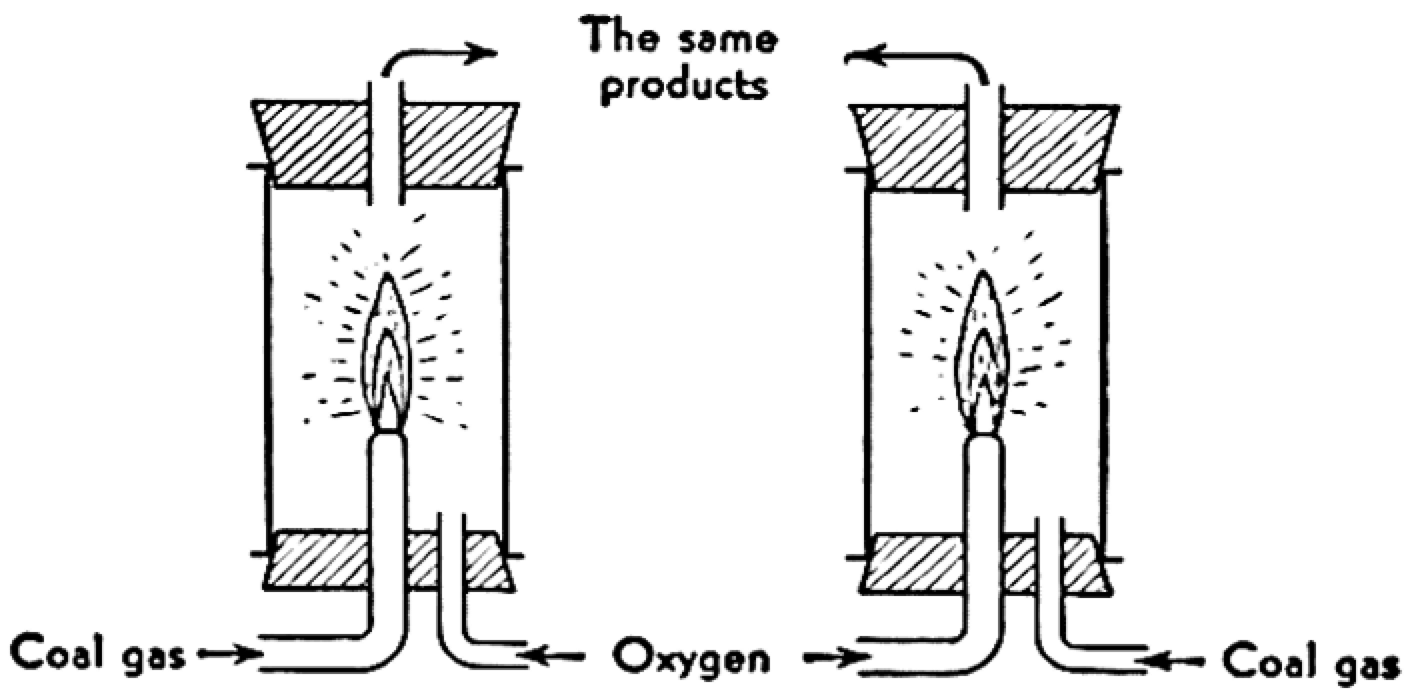


FIG. 17. Coal gas burns in oxygen; oxygen burns in coal gas. This is combustion, a mutual contract.

heat and (3) light. This fact requires a correct statement of combustion in equation form to contain this production of energy. Since it is for the heat produced that most combustion is set in operation, this energy is listed as heat. Thus

$$\text{Carbon} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{heat}$$

To the chemist this statement deals with the two kinds of quantities: matter, which can be weighed—the carbon, oxygen and carbon dioxide—and heat, which is not weighed but measured by means of a thermometer. Each kind is important. Heat is an essential to daily life, and plants must have carbon dioxide in order to grow and to become food for the animal kingdom.

The term combustion is too frequently used to describe the phenomenon in a one-sided manner; for example, to say that coal burns rather ignores the oxygen which is so necessary for this burning. This is, of course, natural since we see the glowing coal and do not see the oxygen. Rather is it a union of coal and oxygen at the surface of the coal. It is usual to see a jet of coal gas burn-

ing in an atmosphere which contains oxygen. If, however, the roles are reversed and oxygen issues from the jet into a container filled with coal gas, the flame is just as visible and all the products are the same. It is, of course, quite unnecessary to be pedantic about it; but it should be remembered that combustion is like a contract—there must be at least two parties to it.

In thinking of the examples of combustion which we have experienced, we notice that different quantities of matter have been involved with consequent differences in the light and heat evolved, for example, a burning match and a blazing bonfire. Sometimes, also, the rate of combustion varies, so that we may speak of slow as opposed to rapid combustion. A pile of refuse may suddenly burst into flame without any apparent cause; we call this *spontaneous* combustion. But normally a state of combustion has to be brought about, as by a match or a spark; fortunately combustible materials just do not go off on their own. To initiate combustion, it is necessary to raise the material concerned to the "ignition point," that is, the temperature at which combustion assumes that rapidity which makes the light and the heat noticeable.

When a state similar to combustion is attained, but perhaps without visible light and no sensible production of heat, we call it *oxidation*. This is the general name applied to all reactions involving oxygen, and combustion is merely a special case of oxidation. A simple example is the so-called burning of our foods in our bodies. No light has ever been noticed, and the large amount of heat actually produced is used in maintaining body temperature and is given off to the surrounding atmosphere. Too frequently we fail to appreciate oxidation because the sensible production of heat is lacking. Those processes which, proceeding very, very slowly, dissipate into their surroundings the heat which in a fireplace or engine would be so apparent are of far greater importance in the quantities of matter involved than all the huge furnaces of various kinds which are a part of our industrial organization.

48 Atmospheric Oxygen

In the atmosphere, in the soil, in the waters of lakes and streams gaseous oxygen is continuously engaged in the slow combustion or oxidation, as it can be more accurately called, of decomposing matter of vital origin, both animal and vegetable. And concerned largely in this process are groups of agents, some living and called

bacteria, others of a similar chemical composition but not classed as living organisms and known by the general and unsatisfactory title of enzymes. The enzymes are responsible for the decay of the tissues of once-living matter. Nature thus provides her own scavengers so that the products of life can be utilized again in her farsighted economy. The extensive swamp and jungle areas of the world provide a suitable locale for the decomposition of worn-out plant life, giving rise in some areas to peat beds. Animal refuse and sewage carried downwards in rivers are much more rapidly decomposed and oxidized bacterially with the aid of atmospheric oxygen dissolved in the waters than is generally realized. Of course where several large neighboring cities pour their sewage into the same river sufficient time may not elapse for complete oxidation, and the inhabitants of such cities as are downstream may complain with good cause.

OZONE AND HYDROGEN PEROXIDE

Two simple oxidizing agents related to oxygen are described below.

49 Ozone

Traces of ozone may be detected in the air surrounding electric motors during their operation. A satisfactory method of preparation is to pass a current of pure oxygen between electrically charged

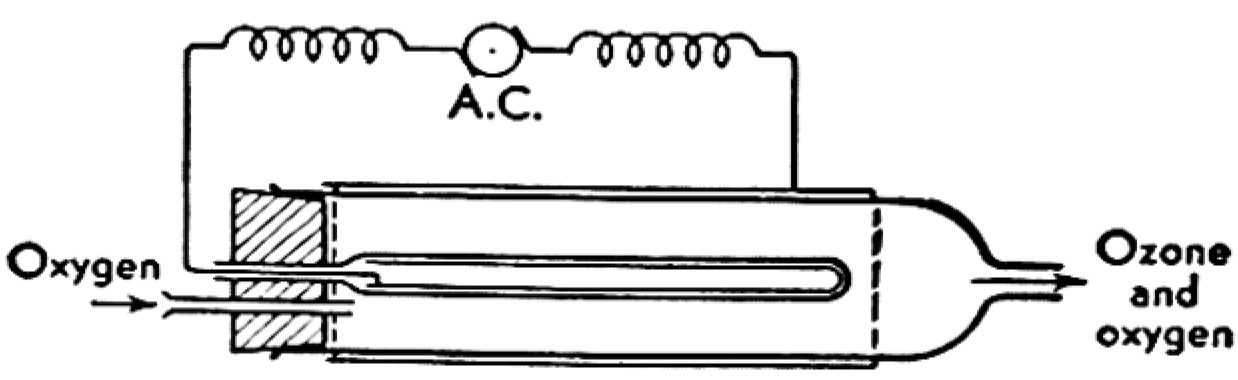


FIG. 18. A simple ozonizer.

plates of glass, across which passes a silent electric discharge. This is the general principle on which large generators of ozone (ozonizers) as well as small demonstration ozonizers are operated. The result is to transform a part of the molecular oxygen into the triatomic ozone, according to the equation in which E (energy) = 69,000 calories:

$$3O_2 + E \rightarrow 2O_3 \tag{1}$$

This may be verified by analysis.

The current of gas leaving the ozonizer contains not more than 15 per cent of ozone, the remainder being unchanged oxygen. Under the conditions of preparation a larger proportion of ozone than the above is unusual because this compound is easily decomposed back into oxygen, in conformity with the equation:

$$2O_3 \rightarrow 3O_2 + E \tag{2}$$

Equation[1] 1 indicates that addition of energy to oxygen is necessary to the production of ozone, called, therefore, an *endothermal*[2] compound (= heat in). In equation 2 ozone is seen to change back to oxygen with the evolution of the same quantity of energy previously absorbed in its formation. Such a reaction as this is called *exothermal.* Equations 1 and 2 may be incorporated thus:

$$3O_2 + E \rightleftharpoons 2O_3 \tag{3}$$

implying the existence of reversibility in chemical reactions. It is generally considered that all chemical reactions are reversible in theory, even if conditions are unfavorable to their reversion. To indicate this state, where both the formation and decomposition of ozone appear to be going on side by side, we say that the two separate reactions are in equilibrium and also that oxygen and ozone, in this instance, are in equilibrium each with the other. This affords an excellent example of chemical equilibrium.

Ozone is a colorless gas with a penetrating odor, and is liquefiable much more readily than oxygen, that is, at a much higher tem-

[1] Chapter 8 contains a full account of how we use abbreviations in expressing chemical changes, and it may be studied, in part at least, before the student proceeds further with the present chapter. These abbreviations consist of a *symbol* for each element (hydrogen, H; oxygen, O, etc.). A subscript number tells the number of atoms of an element which are joined together (O_2, H_2, O_3). A group of different symbols (H_2O) is a *formula*. Symbols and formulae are together represented in an equation ($3O_2 \rightarrow 2O_3$), and an equation tells us in shorthand what chemical change is taking place. Energy is represented by the symbol E; when we wish to be more specific we use the word "heat" or some number followed by the word "calories."

It is unnecessary to memorize symbols, formulae and equations since they are remembered by frequent study.

The equations which follow are numbered for reference purposes.

[2] Energy is always represented in chemical equations in terms of heat (Greek, *thermos*) even though electrical or other forms of energy may be used in a reaction. The different forms of energy are interrelated and may be expressed in terms of one another.

perature. It also is quite unstable, giving up oxygen readily to bodies capable of using it. It is thus a simple and efficient oxidizing agent, a fact which may be shown by the equation

$$O_3 \rightarrow O_2 + O + 32{,}000 \text{ calories} \tag{4}$$

That is, ozone on decomposing gives rise to ordinary oxygen (molecular O_2 such as occurs in the atmosphere) and also to single atoms of oxygen, which are very active and will unite with substances capable of receiving them far more readily than molecular oxygen. Such atomic oxygen is called *nascent*, indicating that at the moment of "birth" it is far more active than later when the atoms, for want of something else with which to unite, unite with themselves to form an ordinary molecule:

$$O + O \rightarrow O_2 \tag{5}$$

The decomposition of ozone into ordinary oxygen, which is so rapid in the presence of bacteria, its existence as a gas at ordinary temperatures and its harmlessness generally make it of great value in purifying and deodorizing the air of large buildings. Air or oxygen containing ozone may be tested by means of a piece of paper moistened with a mixture of starch and potassium iodide in water. The gas containing ozone will show a blue coloration on the paper.

50 Hydrogen Peroxide

Oxygen forms two hydrides, water and hydrogen peroxide, H_2O and H_2O_2. The prefix *per* indicates that this compound contains a larger amount of oxygen than the saturation of hydrogen requires. It may be prepared from barium peroxide and dilute sulfuric acid:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2 \tag{6}$$

It is prepared commercially by electrolysis. When pure, this is a liquid with physical properties closely analogous to those of water. Its chemical properties, however, are reminiscent of those of ozone. When tested with starch-potassium iodide paper it gives a blue coloration, and it decomposes rather readily on being heated or when treated with powdered metals, etc. This decomposition occurs with the evolution of much heat and it readily passes on the

excess oxygen to substances capable of uniting with nascent oxygen. Thus

$$H_2O_2 \rightarrow H_2O + O + E \tag{7}$$

This exothermal decomposition points to hydrogen peroxide as being an endothermal compound. This example as well as ozone would appear to indicate that endothermal compounds are very reactive chemically and also none too stable.

Dilute solutions of hydrogen peroxide in water (about 3 per cent) are much used as a bleaching agent. Concentrated aqueous solutions of hydrogen peroxide are more stable than the dilute, which require a stabilizer or anti-catalyst to inhibit the decomposition. For this purpose acetanilide is used—an excellent example of a catalyst used to retard rather than to accelerate a chemical reaction. Acetanilide thus acts counter to the manganese dioxide used to prepare oxygen from potassium chlorate.

51 Review of Definitions

An oxidizing agent of the simplest type is a substance which gives oxygen to another substance capable of utilizing it.

An exothermal reaction is one which proceeds with the evolution of heat or other form of energy.

An endothermal reaction is one to which energy must be added before it can proceed.

Electrolysis is the decomposition of a chemical compound by the electric current.

An oxide is a chemical compound between oxygen and another element.

Combustion is the chemical union of two substances (one of them generally oxygen) with the formation of one or more different substances and with the evolution of heat and light.

A catalyst is a substance added to a chemical reaction to influence the rate at which the reaction proceeds.

Nascent is the term applied to an element when it has just been liberated from union with some other element and has not yet formed a new union; it is then very active.

52 Summary

Water may be decomposed by (1) the electric current and (2) by some metals to give hydrogen as one of the products; oxygen is the other product in (1).

Hydrogen may also be prepared when certain metals and certain acids interact.

Oxygen may be prepared (1) most abundantly by the liquefaction of air and (2) by the decomposition of certain oxides and compounds containing a large proportion of oxygen.

The physical properties of hydrogen and oxygen are very similar; but the chemical properties are antithetical.

All substances which burn in air burn more rapidly in pure oxygen. Most such substances form oxides when so doing, the non-metals forming acids later on contact with water.

The decomposition of potassium chlorate by heat is hastened by the presence of manganese dioxide, a catalyst; the decomposition of hydrogen peroxide is delayed by the presence of acetanilide, a catalyst. Catalysts may therefore accelerate or decelerate a reaction.

Combustion, a union involving at least two substances and giving out heat and light, is a visible form of oxidation; it is always exothermal. Such unions may be slow or rapid. Spontaneous combustion is a special case.

The preparation of ozone illustrates a reversible reaction which results in an equilibrium.

Questions

1. Describe the electrolysis of water.
2. What does the electrolysis of water prove?
3. By what different methods may hydrogen and oxygen be prepared?
4. Contrast the physical properties of hydrogen and oxygen.
5. Define in your own words the terms oxide, catalyst, decomposition, spontaneous.
6. Explain what is involved in the process of combustion.
7. Name all the circumstances you can in which (*a*) heat, (*b*) light and (*c*) both heat and light are produced in nature and artificially.
8. Can a chemical reaction occur without the presence of energy?
9. Is the boiling of water a chemical reaction? Why?
10. What do you conclude from the fact that different metals require different conditions in order to decompose water?
11. What is the difference between an oxide and a hydroxide?
12. Compare, in tabular form, the properties of ozone and hydrogen peroxide.

The Atmosphere

53 The Breath of Life

Next to water in importance in our natural surroundings, the atmosphere demands consideration; the ancients regarded it as one of the four primal elements. Without giving the word *element* the significance they gave it, we can see how greatly the earth, air, water and fire influenced all their conceptions of living matter. Small wonder, too, that the sun was worshiped for centuries as the greatest of all the deities, when it is realized that without its heat and light coming to us through the atmosphere no life could exist on our planet. Yet for all its antiquity, the atmosphere defied attempts to investigate its exact composition until less than sixty years ago. That it is indeed the breath of life was demonstrated by Lavoisier a century and a half ago, and it is for his explanation of the role of oxygen in respiration that he has been called the "Father of Physiology."

The various constituents of air are classified in Table 2.

TABLE 2

Slightly Variable Constituents	*Most Variable Constituents*
Oxygen, about 20 per cent by volume	Water vapor
Nitrogen, about 78 per cent by volume	Dust, ammonia
Rare gases, about 1 per cent by volume	Sulfur dioxide
Carbon dioxide, about 0.03 per cent by volume	Hydrogen sulfide
	Ozone, etc.

54 The Importance of Air

Some of the constituents of air have definite functions. Oxygen supports combustion, that is, the burning of fuels, respiration of animals, oxidation of decaying matter, whether vegetable or

animal, and the many other chemical changes which require its presence. The rare gases appear to have no special function. Nitrogen is useful in diluting the oxygen, which would otherwise cause too rapid combustion; it also serves to enrich the soil. Carbon dioxide, though small in proportion, is vital to the vegetable kingdom and, in the great mass of the atmosphere, is present to the extent of thousands of tons over every square mile of the earth's surface. It is produced by the continuous oxidation of carbon-containing compounds and is removed by the continuous demand of plant life. Though local conditions may vary greatly, its proportion shows very slight variation.

55 Atmospheric Water

Water vapor, variable within very wide limits in the atmosphere, comes from the evaporation of large bodies such as oceans, lakes and rivers which are swept upwards only to descend later in the

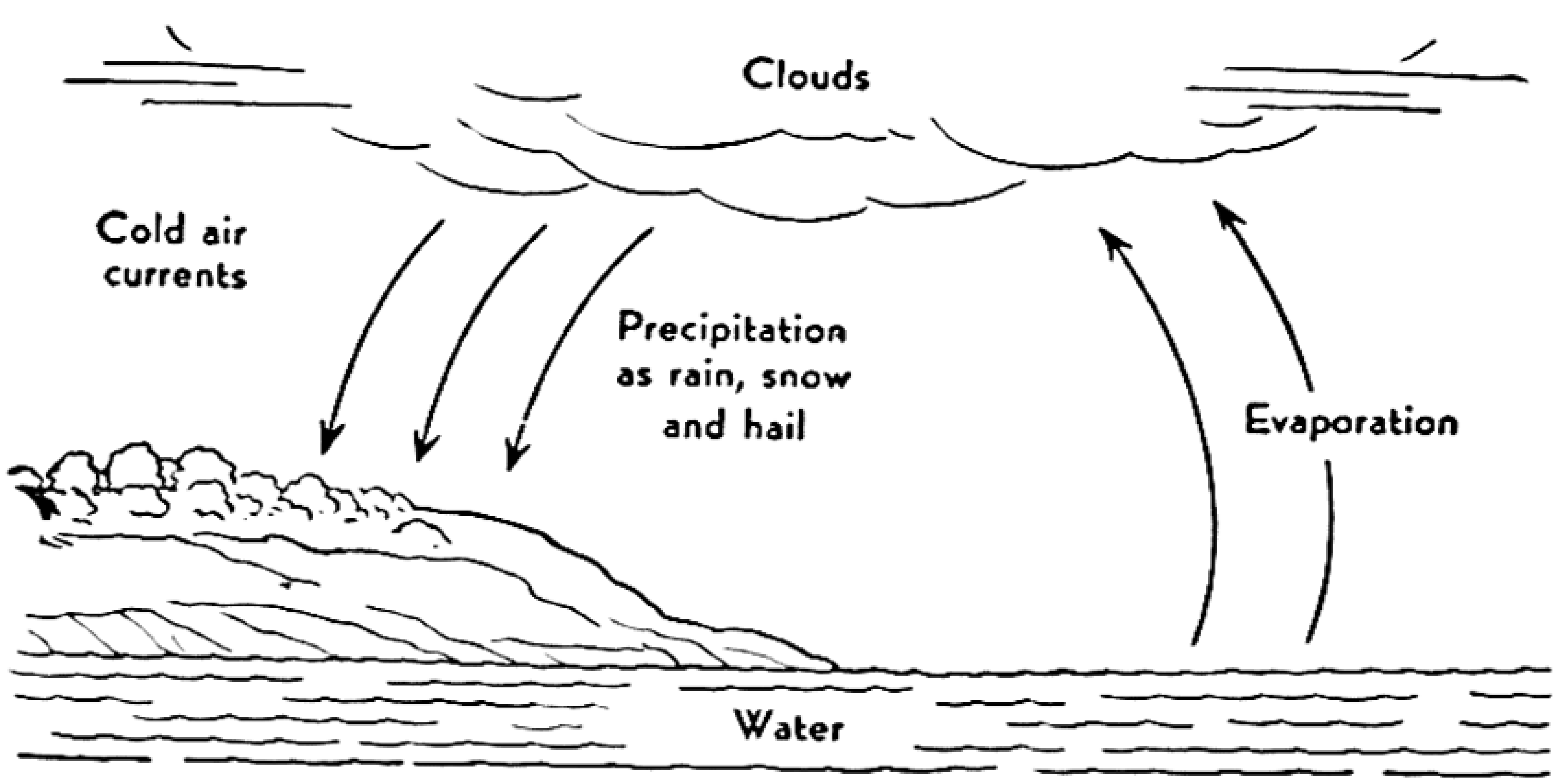


Fig. 19. Evaporation and precipitation—nature's water cycle. Plants need water, we use plants—we are parasites.

same or distant regions as dew, rain, snow or sleet, depending upon local conditions. As the sun dips below the horizon the earth loses much of the heat it has received during the day, and the moisture in the atmosphere condenses on cold surfaces as dew. When the atmosphere contains a relatively large proportion of water and a current of cold air rushes in upon it, condensation in the upper levels results in the formation of droplets which may descend as rain or solid water particles, depending upon how cold the atmosphere happens to be. The presence of clouds indicates dif-

ferences in temperature between atmospheric levels. Fog is merely droplets too small to descend rapidly and too large to be invisible; dust particles aid as centers for the condensation of water vapor.

56 Humidity

On a hot, sticky day in summer the water vapor content of the atmosphere is large; on a cold winter day in the dry prairies the atmosphere is sparklingly clear and free from such quantities. There is thus a maximum amount of water vapor that the atmosphere can hold before precipitation, and the amount is greater for warm air than for cold. The proportion of water vapor actually in the atmosphere (at any time) to that which the atmosphere can hold is known as the relative humidity. We can therefore expect a greater humidity near lakes than in deserts, and in warm climates than in cold; but the relative humidity depends on both factors, the temperature and the quantity of water. Too low a humidity increases the rate of evaporation from the body surface, thereby causing the sensation of cold. Equally uncomfortable is too great a humidity, which lowers this rate beyond that to which the body is accustomed. The optimum humidity is that at which normal evaporation from the body surface, including the mucous membrane of the nose, throat and lungs, proceeds unhindered. If the temperature of a room is 70°F, the most suitable humidity is about 47 per cent, that is, 47 per cent of the 18.2 mg of water per liter that air can contain at that temperature. This works out to about 8.5 mg per liter, or a little over one pound of water for a room 20 feet by 10 feet by 10 feet. Too low a humidity in a room is not merely uncomfortable for the occupants but causes shrinking of hardwood floors, furniture and woodwork generally. A continued excess of humidity is noticeable in causing doors and wooden drawers to jam.

Because of the necessity of ventilation, especially in cold weather, houses should be continuously supplied with moist air to replace the water vapor that is lost to the outside and to make up the deficiency in moisture in the cold, entering air.

That the atmosphere contains some moisture at all times may be demonstrated by exposing to it a few lumps of calcium chloride in an open dish. In a few minutes water collects on the surface of the lumps, which tend to dissolve in the absorbed liquid. Such a sub-

stance as calcium chloride is called *hygroscopic* because of this property. This substance is frequently sprayed on dirt roads, where, by its absorption of moisture, it prevents the spread of dust. Another such substance is glycerin, which in hand lotions absorbs moisture from the air and prevents chapping (or cracking) of the skin through excess dryness.

57 Air and Plants

Plant life is dependent very largely on the quantities of carbon dioxide and water in the atmosphere. Both are necessary to growth, but water is utilized to the greater extent. Trees retain and use such huge quantities of water that their destruction prevents its retention in the soil and upsets the water balance to such an extent that floods are to be anticipated, as in China and elsewhere, where the hillsides pour down into the already wet valleys more than the rivers can carry away. And not merely are the large trees important to flood-prevention. Prairie land without grass can no longer hold water, with the result that the first windstorm that arrives carries away with it tons of rich topsoil, leaving a barren waste behind. This has become a serious problem on the American continent. This topsoil, weathered by centuries, is just suited to the growth of plants for human and animal food and it cannot be replaced until nature has weathered the soil left behind, or until thousands of tons of fertilizers have been put on to duplicate what has been swept away.

58 Respiration

In human respiration about one quarter of the oxygen admitted to the lungs at each inspiration is converted to carbon dioxide, thus increasing the percentage of the carbon dioxide in the atmosphere enormously. The upper limit set by experts in ventilation for carbon dioxide content is 0.1 per cent by volume, or three times that normally present. The maintenance of this standard requires frequent renewal of the air in a crowded room, the frequency being determined by the cubic content of the room and the number of occupants. The air conditioning of homes, offices, theaters and other buildings where people gather must therefore involve removal of dust particles by washing, the proper heating and moisture control, the elimination of excess carbon dioxide and the replenishment of oxygen.

59 Air as a Liquid

If the variable constituents, together with carbon dioxide, are removed from the air, the residue, consisting of oxygen, nitrogen and the rare gases, may be subjected to a process known as liquefaction (see Fig. 20). This process consists chiefly in a series of compressions and expansions with loss of heat until finally a liquid drips from the liquefaction apparatus. It is liquid air, a pale bluish liquid boiling at a very low temperature (−196°C) and itself composed of oxygen and nitrogen. This liquid is fractionated,

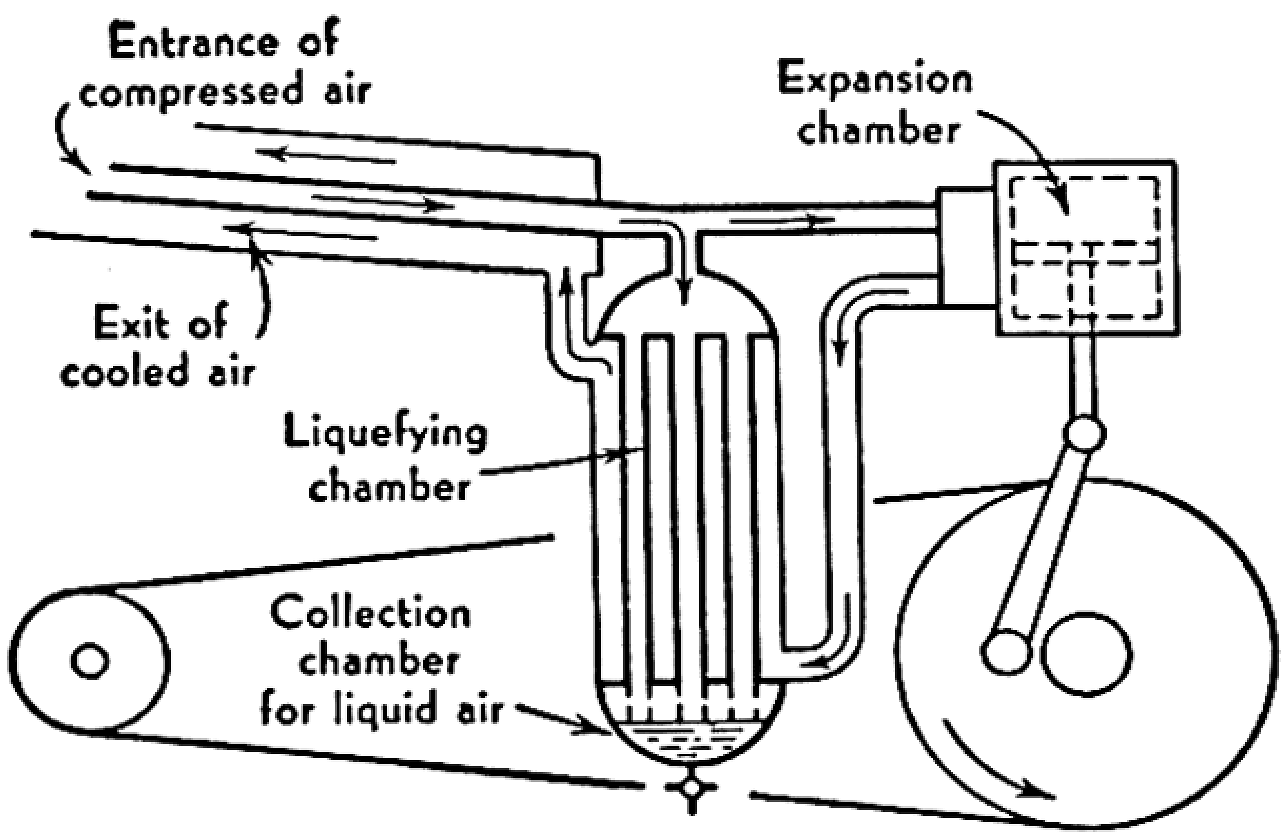


FIG. 20. Liquefying the atmosphere.

that is, portions of it are allowed to boil off and are subsequently collected. In this way pure oxygen, nitrogen and the different rare gases—argon, krypton, neon and zenon—are obtained separately. It is the modern method of preparing these gases in large quantities, and, when stored in strong steel cylinders under great pressure, they are available for their many separate uses.

60 Air Is a Mixture

That air is a mixture of several different elements and compounds is seen from the above, for by purely mechanical means it is possible to remove each component individually. In this mixture each constituent is identifiable separately and is capable of carrying on its individual reactions independently of the others. The two most important constituents, nitrogen and oxygen, are present in a ratio that corresponds to that of no known compound of the two. In any case, a slight decrease in, say, the oxygen proportion does not appreciably change the behavior of this mixture. This

variation in composition is just *not* true of a chemical compound which is absolutely invariable in its composition. The normal composition of air may be ascertained simply by passing a known volume of it over certain reagents and measuring the decreased volume at each stage. Thus concentrated sulfuric acid will remove the water vapor, and sodium hydroxide the carbon dioxide, leaving a mixture of oxygen, nitrogen and the rare gases. If in this mixture a small piece of yellow phosphorus is allowed to burn, it will remove the oxygen, leaving only nitrogen and the rare gases. This kind of procedure enabled Cavendish, a contemporary of Priestley, Lavoisier and Black (who discovered carbon dioxide), to have within his grasp the mystery of the rare gases. A century later it fell to Rayleigh and Ramsay to finish Cavendish's work by their fractional distillation of liquid air.

61 Atmospheric Impurities

These are the constituents not normally present. They are the products of local conditions.

Chief among them are solids such as fine particles of unburned carbon in smoke from chimneys and particles of sand raised by high winds traveling over dry soil or by vehicular traffic. Smoke has become such a nuisance in large cities as to call for municipal regulation. Both smoke and sand are injurious to the human lungs, especially since they may be accompanied by noxious bacteria.

Smelters burning metal pyrites, which contain sulfur, evolve large volumes of sulfur dioxide. Though a good germicide, sulfur dioxide nevertheless has a detrimental effect on crops in the neighborhood. The same gas is continually being evolved from active volcanoes. Fortunately, however, it is quite soluble in water so that the seas, lakes and rivers can absorb it before it becomes too widely present. Hydrogen sulfide likewise is given off from cavities in the earth's crust, such an evolution occurring suddenly in 1896 with fatal results to the workmen excavating for a lighthouse in Chesapeake Bay. Ammonia is produced wherever animal matter is permitted to decay, as in manure piles. It is extremely soluble in water and so is carried into the soil by the rainfall. Actually these three gases, sulfur dioxide, hydrogen sulfide and ammonia, are produced in such small quantities as to make their content in the whole atmosphere negligible; but locally they may

constitute a decided nuisance. Ozone is always produced in small amounts during electrical storms.

Traces of bacteria may occasionally be found in the atmosphere in congested sections, and in the country the pollen from plants during certain seasons, though small in amount, can be of great discomfort to those who suffer from hay fever. These two impurities are negligible in quantity and unimportant chemically, however important they may be from the medical standpoint.

62 Nitrogen Fixation

As far as animal respiration is concerned, nitrogen serves to dilute the oxygen in the atmosphere. But compounds of nitrogen are essential to both animal and vegetable life, nitrogen being one of the most important constituents of living cells. Since all animals depend upon the vegetable kingdom for their foods, they obtain nitrogen directly from plants, which in turn receive their necessary nitrogen mainly from nitrogen compounds (ammonia and nitrates) in the soil. Certain plants, such as peas and beans, have the unique power of extracting the free, inert nitrogen from the atmosphere and incorporating it into their chemical composition. This they accomplish by means of the small nodules on their roots. The ripened fruits may be picked to serve as food rich in nitrogen for the benefit of the animal creation, or the whole plant may be ploughed under and, by its decomposition, may provide the necessary combined nitrogen for the next season's growth of the same or other plants. This process of trapping an elusive gas and combining it to produce compounds which may be easily handled and used is called *fixation.*

NITROGEN AND ITS COMPOUNDS

63 Occurrence

In spite of the large amount of nitrogen in the atmosphere the main sources of nitrogenous materials up to thirty years ago were the nitrates of sodium and potassium obtainable from Chile and Germany and ammonia produced in the destructive distillation of coal (§ 463). That situation is now completely altered by the liquefaction of air, the synthetic fixation of atmosphere nitrogen by improvements in the Haber process and the oxidation of ammonia to nitric acid.

64 Preparation and Properties

Nitrogen does not display such spectacular properties as chlorine, hydrogen and oxygen. It is without color, odor and taste, almost altogether insoluble in water and combines only with very active substances under special conditions. Its liquefaction point is $-196°C$, whereas that of oxygen is $-183°C$; thus from a mixture of these two in the liquid state nitrogen will boil off first. This is the chief method of preparation.

For laboratory use, small quantities of nitrogen may be prepared by heating together a mixture of ammonium chloride and sodium nitrite:

$$NH_4Cl + NaNO_2 \rightarrow NaCl + 2H_2O + N_2\uparrow \qquad (8)$$

The gas can be collected over water since it is practically insoluble in it.

Tests will demonstrate the inert character of nitrogen; it will not burn or support the combustion of carbon, sulfur, etc.

Although nitrogen is almost insoluble in water, it does under pressure dissolve to a sufficient extent to cause considerable discomfort and even death to divers and others who breathe air under pressure. As the air pressure is decreased during their rise to the surface, this nitrogen comes out of solution and forms pockets of gas in the blood vessels. This condition, called the *bends*, is alleviated by slowly reducing the pressure so that the nitrogen may be evolved from the lungs in the normal way.

That nitrogen is a sluggish element is obvious; but it must not be classed with the rare gases, helium, argon, neon, etc. They do not form any chemical compounds as we know them, whereas nitrogen does—if sufficiently stimulated to do so. Magnesium, for example, when heated in an atmosphere of nitrogen, combines with it to form an amorphous powder, magnesium nitride (Mg_3N_2), which on being added to water produces ammonia (NH_3) and magnesium hydroxide [$Mg(OH)_2$]:

$$3Mg + N_2 \rightarrow Mg_3N_2 \qquad (9)$$

$$Mg_3N_2 + 6H_2O \rightarrow 2NH_3 + 3Mg(OH)_2 \qquad (10)$$

When heated strongly with calcium carbide, nitrogen forms calcium cyanamide, a highly important substance:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \qquad (11)$$

Thus, if sufficient energy is forthcoming, nitrogen will form chemical compounds of considerable importance. Some of them are described in the succeeding sections of this chapter.

65 Ammonia (NH_3)

Ammonia is prepared on a large scale by bringing nitrogen and hydrogen together at a high temperature and pressure and in the presence of a suitable catalyst. This method is the basis of the Haber process and is one of the methods for the fixation of nitrogen (§ 494). Smaller quantities may be obtained by heating any ammonium salt with an alkaline substance:

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3 \uparrow \tag{12}$$

Thus ammonium chloride and sodium hydroxide, when heated together, form sodium chloride, water and ammonia.

The properties of ammonia show it to be a colorless gas with the acrid taste characteristic of alkalies and with a pungent odor. Nitrogenous organic matter undergoing putrefaction evolves ammonia, which is consequently readily detected by its odor. It is extremely soluble in water, the solution taking on its odor. In addition to forming an aqueous solution, some of the ammonia combines to form a loose compound with water, ammonium hydroxide (NH_4OH). Possessing the hydroxyl radical (OH), it has alkaline properties similar to those of sodium and potassium hydroxides, only it is much weaker than they. Ammonium hydroxide combines with acids to form water and compounds such as the chloride (NH_4Cl), sulfate [$(NH_4)_2SO_4$] and nitrate (NH_4NO_3). Ammonia also combines with the same acids by addition, giving the same salts:

$$NH_3 + HCl \rightarrow NH_4Cl \tag{13}$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{14}$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \tag{15}$$

If we inspect the formulae of these compounds we shall notice that the radical NH_4 occurs in all of them. It is known as the ammonium radical, which is incapable of existing alone except as a positively charged ion (NH_4^+).

Ammonia in aqueous solution has considerable application in the industries, and is used in the home for cleansing purposes. Ammonium salts are frequently used in fertilizers. One important

use of gaseous ammonia depends on its ease of liquefaction especially under pressure; at 760 mm it boils at −33°C. If this liquid is allowed to evaporate rapidly, the latent heat of vaporization needed to permit the liquid ammonia to become gaseous is absorbed from its surroundings; thus it finds considerable application in artificial refrigeration units, both large and small.

66 Oxides of Nitrogen

These are six in number and the following table shows a comparison of their chief physical properties:

TABLE 3

Formula	*Name*	*Physical Properties*
N_2O	Nitrous oxide	Gas, colorless, sweet-smelling, anesthetic
NO	Nitric oxide	Gas, colorless, sharp odor
N_2O_3	Nitrogen trioxide	Liquid, bluish, unstable, decomposing to NO and NO_2
NO_2	Nitrogen dioxide	Liquid, reddish brown, pungent
N_2O_4	Nitrogen tetroxide	Liquid, reddish, stable below 0°C, decomposing above 0°C to NO_2
N_2O_5	Nitrogen pentoxide	Solid, white, crystalline

Nitrous oxide is a colorless gas with a faintly sweet odor, slightly soluble in water. It is easily liquefied and may be stored in steel cylinders. Because on inhalation it produces a feeling of exhilaration, it is known as laughing gas. When mixed with oxygen it is used as an anesthetic. If tested with a glowing splinter, it sets the splinter alight much as oxygen, since it gives up its oxygen easily to the carbon and hydrogen compounds of the wood.

Nitrogen pentoxide when dissolved in water gives rise to nitric acid.

67 Nitric Acid

Chili saltpeter ($NaNO_3$) when heated with concentrated sulfuric acid (see Fig. 21) evolves a clear liquid containing some brown fumes of NO_2:

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3 \uparrow \qquad (16)$$

The nitric acid of commerce is about 70 per cent pure, the rest being water. It is not merely a strong acid; it is at the same time

a powerful oxidizing agent since it decomposes under favorable conditions to evolve oxygen and some of the oxides of nitrogen. Indeed all nitrates are decomposed by heat.

Like other acids, nitric acid neutralizes an alkali, forming a salt and water:

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \qquad (17)$$

The sodium nitrate so formed is unstable to heat as is potassium nitrate (KNO_3), one of the ingredients of common gunpowder.

Unlike most acids, nitric acid reacts with metals with decomposition of its own molecule. The particular metal, the concentration and the temperature of the acid influence the final products. One of its reactions with copper, for example, is

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O \qquad (18)$$

Zinc with nitric acid may even produce ammonia.

Besides reacting with alkalies and metals, nitric acid readily attacks such materials as cotton, silk and wool, forming compounds with them. By its action on certain carbon compounds, nitric acid is extremely useful in the manufacture of such widely different articles as artificial silk, explosives, dyes and medicinals.

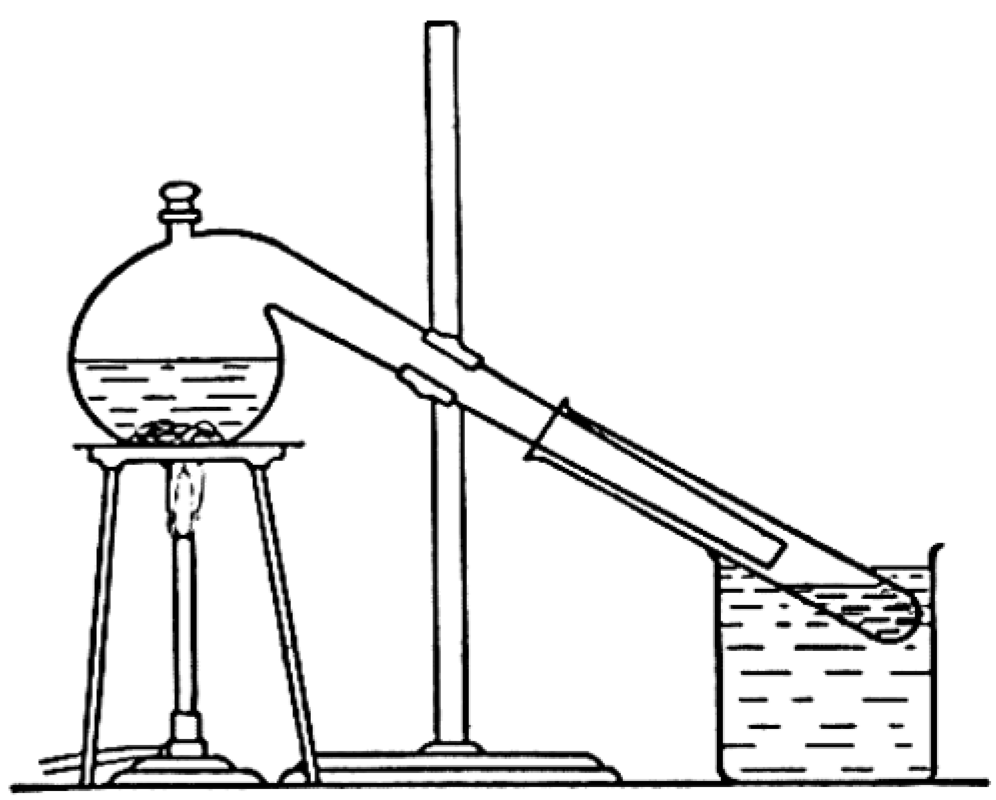


FIG. 21. Laboratory preparation of nitric acid from sulfuric acid and sodium nitrate.

Nitric acid is being manufactured more and more by fixation of nitrogen processes. One method is the catalytic oxidation of ammonia (§ 495), another is the direct union of nitrogen and oxygen in the electric arc, where nitric oxide and nitrogen dioxide are produced. These oxides on dissolving in water give appreciable quantities of nitric acid.

The advantages of utilizing the atmosphere for the manufacture of ammonia and nitric acid are such as to render any country not possessing natural supplies of nitrates independent during peace and war, nitric acid being indispensable to industries concerned with dyes, fertilizers, nitrocellulose, nitroglycerin, T.N.T., etc.

68 Review of Definitions

"Hygroscopic" describes the ability of a substance to absorb moisture from the surrounding atmosphere.

Respiration is the process of taking in (inspiration) the atmosphere and exhaling it (expiration) so that one, at least, of its constituents may be utilized by living cells.

Fixation is a process whereby a gaseous substance is rendered relatively non-volatile or solid so that it may be stored for active chemical use.

"Inert" describes a substance which shows no chemical activity under ordinary circumstances, for example, nitrogen, the rare gases.

69 Summary

Air is a mixture of many gases, but principally of nitrogen, oxygen, carbon dioxide and water vapor.

Both plants and animals breathe. Plants take in carbon dioxide during daylight and give out oxygen, whereas at all times animals take in oxygen and give out carbon dioxide. These functions (which are complementary) constitute respiration.

At a low temperature air may be liquefied, and from this liquid the separate gaseous constituents may be obtained by fractional (selective) distillation.

Water vapor is a necessary though variable constituent of the atmosphere. It is important for (1) the growth of plants and (2) the respiratory comfort of animals.

Relative humidity is the percentage of water which the atmosphere contains calculated on the basis of how much it can contain at that temperature and pressure.

Though inert, nitrogen can be "fixed," that is, forced to combine with other elements, such as oxygen and hydrogen, to form ammonia and nitric acid eventually.

Questions

1. If primitive tribes worshiped the sun, moon, planets, etc., why were there no air-worshipers?
2. Name the chief gaseous constituents of the atmosphere, and state the approximate proportion of each.
3. What is the importance of water vapor in the atmosphere? How can you prove its presence?
4. Apart from the demands of living matter, what use is made of the atmospheric constituents?
5. Outline briefly the utilization of oxygen, nitrogen and carbon dioxide by living matter.
6. What factors combine to keep the atmosphere constant in its content of oxygen and carbon dioxide?
7. Why should the air in homes need more humidity in cold climates than in warm?
8. How may the nitrogen content of the soil be replenished by growing plants?

6

Gases

70 Law-Abiding Subjects

The gases studied so far include water vapor, oxygen, nitrogen and hydrogen, which are colorless, odorless, tasteless and invisible. Their presence can be ascertained only by subjecting them to tests which provide visual evidence of their existence. In spite of their seemingly intangible nature, however, it is about this gaseous state of matter that we actually know most, since their simple structure and almost perfect obedience to certain natural laws have made them fitting subjects for intensive study.

Later we shall study gases which possess color and odor; but there are certain physical characteristics common to all gases. The first of them is their ability to fill any ordinary space or container in which they may be set free, whereas a piece of iron remains in a rigid position wherever placed, and a liquid, such as water or mercury, flows in such a way as to find a position nearest to the center of the earth. This ability to travel or diffuse rapidly which is characteristic of gases may be easily illustrated by setting free a quantity of a gas, such as ammonia, in one corner of a large room. In a remarkably short time it may be detected equally in all parts of that room. This indicates that a volume of any gas must be composed of a large number of very much smaller parts which can move rapidly in all directions. This quality of gases is expressed in what has been called *the kinetic-molecular theory*, which states that gases are composed of small separate particles called molecules, these molecules being in a state of rapid motion. The rapidity of this motion and the dimensions of the space occupied by a gas are determined by two factors, temperature and pressure; and it is with the effects of these factors that the so-called gas laws deal. These gas laws are discussed here in their historical order.

71 Boyle's Law

About the middle of the seventeenth century Robert Boyle interested himself in an experimental study of the atmosphere, though he was not aware that it is a mixture of several gases. To

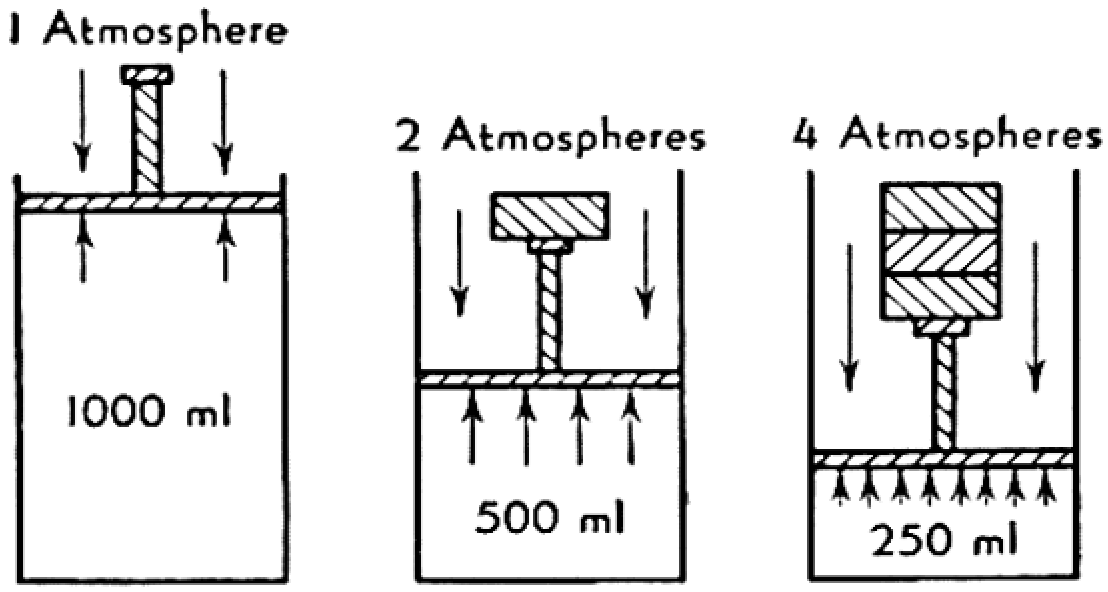


FIG. 22. Illustrating Boyle's law.

him it was an elastic fluid. The results of his experiments may be demonstrated as follows.

Suppose we have a cylinder containing a volume of gas and fitted closely with a frictionless and weightless piston, all so arranged that the cylinder and its contents may be kept at any desired temperature and so that weights may be applied to the piston (Fig. 22). Now let the temperature of the apparatus be kept at 0°C and the volume of gas be 1000 ml when no weight is on the piston. Under these circumstances the piston will be seen to stand at some definite height in the cylinder, indicating that it encloses the volume stated. It can easily be shown that there is a pressure caused by the atmosphere which attempts to push the piston inwards; that it does not respond indicates that it is being pushed out equally by the gas from inside. Let us call this pressure from outside 1 atmosphere. Now place upon the piston a weight equal to that of the atmosphere, making in all 2 atmospheres. The piston will at once move downward until it comes to a position of rest. If the volume of the gas is now read with the temperature still at 0°C, it will be found to be half of 1000 ml, that is, 500 ml. Again let us put on more weights so that the total pressure on the piston is now four times that of the atmosphere. The piston will again move

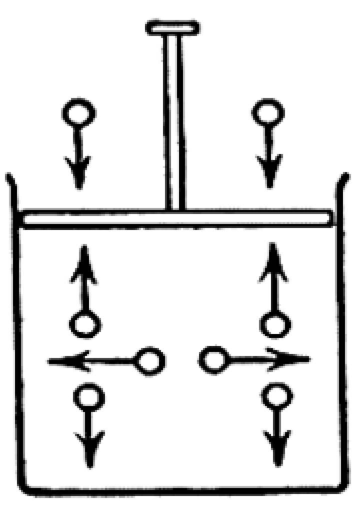


FIG. 23. The molecules of a gas bombard the sides of a container and resist external pressure.

downward until it comes to a position of rest, where the volume is found to be 250 ml.

If these additional weights are now removed successively, the piston moves upward, that is, in the opposite direction, and takes the former positions. If we summarize these observations we shall find certain relationships: (1) the greater the pressure, the smaller the volume; (2) the smaller the pressure, the greater the volume; (3) pressure multiplied by volume gives a constant value. All this is expressed in Boyle's law as follows. *If the temperature remains constant, the volume of a given mass of gas varies inversely as the pressure.* Thus it is seen that, provided no change in temperature is permitted from start to finish in such an experiment, the molecules of gas show a definite resistance to pressure, this resistance increasing as the volume decreases.

Pressure		*Volume*		*Product*
1 atmosphere	×	1000 ml	=	1000
2 atmospheres	×	500 ml	=	1000
4 atmospheres	×	250 ml	=	1000

In practice we cannot continue to compress a gas without some limits being reached, as will be shown in a later paragraph.

If we represent the volume of a gas by V, its temperature by T and the pressure by P, Boyle's law can be stated so:

$$V = \frac{1}{P}$$

when T is constant.

72 Charles's Law

This law, attributed to both Charles and Gay-Lussac, deals with the effect of temperature. To illustrate it, use a cylinder and piston similar to those of the previous experiment (Fig. 24). Let the temperature at the start be 0°C, the pressure that of the atmosphere, which usually remains fairly constant for our purpose, and the volume 273 ml. Now heat the cylinder and its contained gas to 1°C and keep it fixed at that value. The piston will move outwards until it comes to rest at a position which shows the volume to have increased to 274 ml. If heat is again applied until the temperature is 10°C, the piston will again move outward to indicate a new volume of 283 ml. Similarly at a temperature of

100°C the volume will be 373 ml; thus for each 1° rise in temperature above 0°C the volume will increase $\frac{1}{273}$ of its initial volume.

If this heat program is reversed, the piston will be found at −1°C to sink inwards to show a volume of 272 ml, at −100°C a volume of 173 ml, etc. These results may be summarized thus, allowing the piston to move according to the dictates of the enclosed gas: (1) the higher the temperature, the greater the volume;

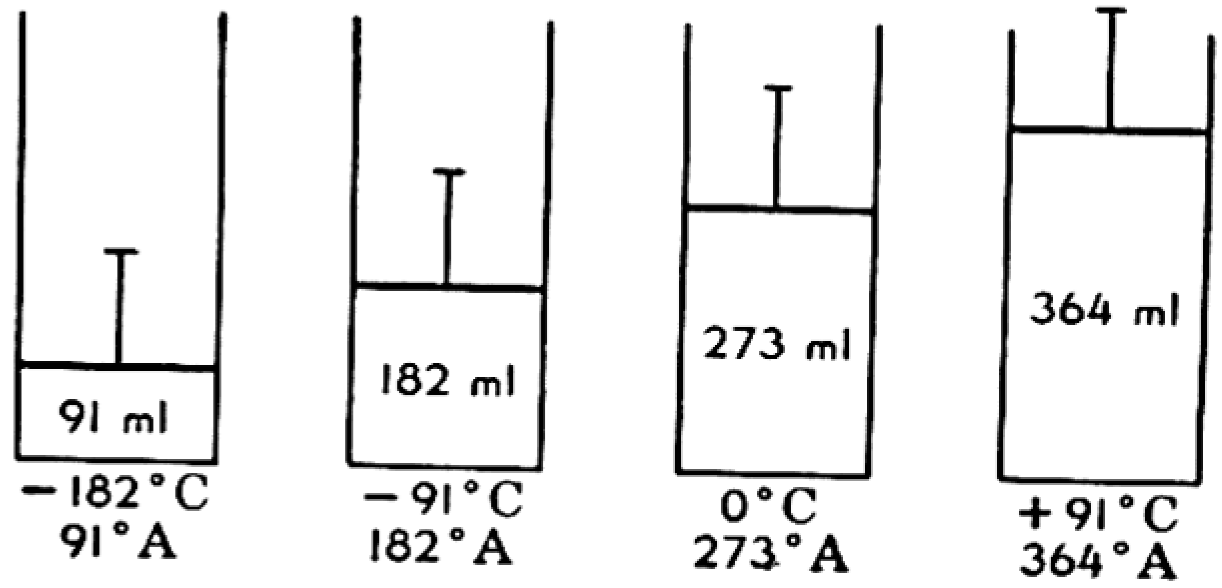


FIG. 24. Illustrating Charles's law at constant pressure.

(2) the lower the temperature, the smaller the volume; (3) the volume of a gas increases or decreases $\frac{1}{273}$ of its volume for each 1° rise or fall in temperature from 0°C.

73 Absolute Zero

Should the temperature be decreased still more in this experiment, it is logical to expect that at −273°C, unless something occurred to prevent it, the gas would have no volume at all, that is, matter would be destroyed. Now this is contrary to the law of conservation of mass. Also, if the temperature were again raised above this −273°C, gas should theoretically appear out of nothing—which again is improbable. Something does occur, however, before this low temperature is attained. The gas, no matter which one it is, becomes liquid, and so the gas laws no longer apply. As a matter of fact, hydrogen has resisted liquefaction down to −259°C and helium as low as −269.5°C. This theoretical temperature of −273° on the centigrade scale is used as the zero of a new temperature scale known as the absolute or Kelvin scale, each degree of which is equal to one degree centigrade. Thus 0°C is 273°K and so on, the °K being found by adding 273 to the centigrade reading. The Kelvin reading eliminates negative readings in calculations. In this system, Charles's law becomes: *The volume of any gas, if the pressure remains constant, varies directly as the absolute temperature.*

Charles's law, like Boyle's law, has one of the three quantities (volume, pressure, temperature) fixed in order that the other two may be varied, but in Charles's law it is the pressure which is kept constant. The usefulness of this law may be shown by calculations.

74 A Variation of Charles's Law

In the above explanation of this law, Fig. 24 shows that the pistons can move, thus keeping the pressure the same inside and

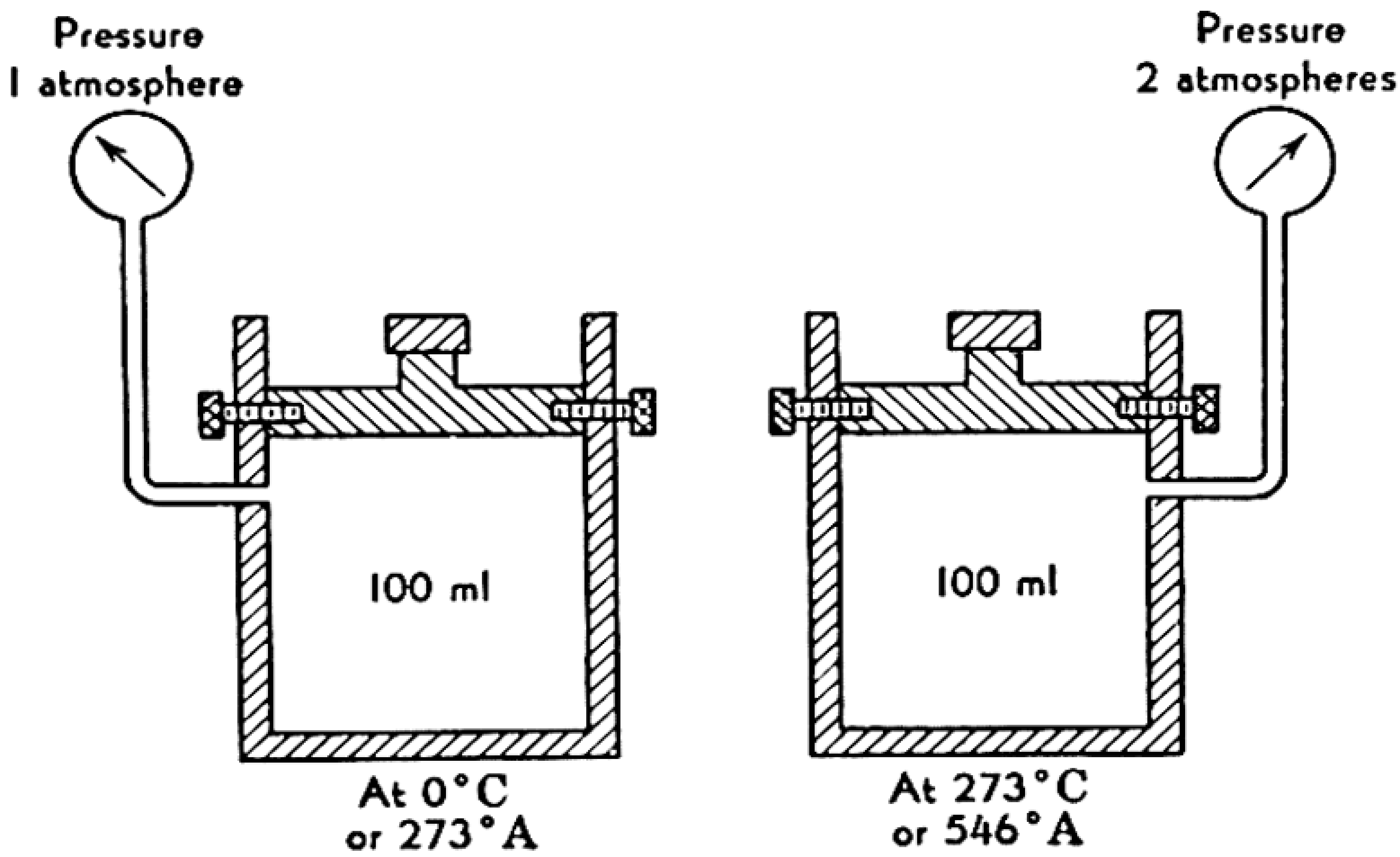


FIG. 25. Illustrating Charles's law at constant volume.

out. If, however, we suppose that the piston is fixed so that it cannot move and no leakage of gas in either direction can take place, we have an interesting variation of Charles's law. It is illustrated in Fig. 25, in which a cylinder with a fixed piston contains 100 ml of gas, having been filled at 0°C and atmospheric pressure (760 mm Hg). Attached to the cylinder by a fine tube is a pressure gauge. Now when the cylinder is heated, the volume cannot increase but the pressure increases and in the same ratio as the volume did previously, that is, $\frac{1}{273}$ of its value for each degree centigrade rise in temperature. Conversely, if the temperature is lowered, the pressure becomes less. As before, the temperatures must be converted to degrees absolute.

75 The Kinetic-Molecular Theory

Observations over a period of time and on a number of different gases led to the formulation of this theory: *A gas is composed of a large number of particles [later called molecules] which are very small*

and in a state of constant, rapid motion. It was known as the kinetic-molecular theory and was designed to explain the behavior of gases towards the application of pressure and of heat as embodied in the laws of Boyle and Gay-Lussac. If the kinetic-molecular idea is correct, we have the following internal picture. When the piston is in a certain position in the cylinder, it is held there, against the pressure from without, by the rapid bombardment of its surface by a multitude of gas molecules from within. Each of these molecules has a certain mass and a certain rapidity of movement or velocity, and the force which each molecule exerts against the piston depends upon this mass and this velocity. Also, the dimensions of the gas volume contain a distance over which a molecule going from the bottom of the cylinder to the piston must pass; this the molecule will accomplish in a certain time. If the piston is forced inward so that the volume is lessened, a molecule now traveling from the cylinder bottom upward to the piston will have a shorter distance to cover and can make many more trips (at the same velocity) in the time it formerly took. Thus the molecules, though hitting the piston with the same force as before, now strike it oftener, that is, they support, or exert, a greater pressure. This shows how the theory supports and explains Boyle's law.

To apply this theory to Charles's law, let us first visualize the situation of a gas at 0°C. There the molecules are moving rapidly in all directions, though in straight lines between collisions, each molecule contributing its force of mass and velocity to the total pressure exerted on the walls of the container. The addition of heat changes this force (mass × velocity), not by changing the mass but by changing the velocity. This change is to increase the velocity very largely since the kinetic energy of a molecule is given by the expression

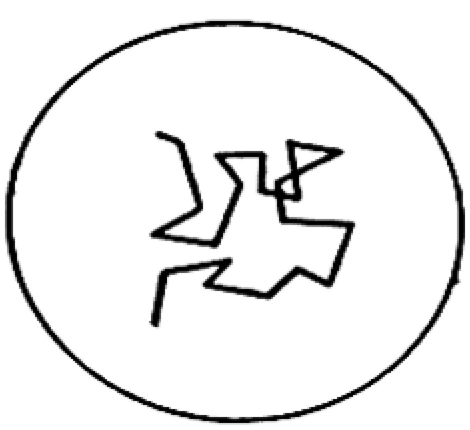


FIG. 26. The Brownian movement—the eternal restlessness of matter.

$$\text{K.E.} = \tfrac{1}{2}mv^2$$

where K.E. stands for kinetic energy, m for mass and v for velocity. The bombardments of the molecules against the sides of the container therefore become more frequent. The pressure increases in proportion in a sealed container, and the

volume increases in proportion if the container is fitted with a movable piston.

Cooling, of course, produces a reverse effect.

Actually this idea of molecular movement was not farfetched for two reasons: first, that a quantity of a colored gas could be seen spreading quickly when mixed with a colorless gas; second, that the botanist Robert Brown had seen under a microscope the movement of very small masses of matter in a liquid medium even though these masses were much larger than molecules, as we now know. This phenomenon has become known as the Brownian movement and is very interesting to watch. (See Fig. 26.)

76 Avogadro's Law

Since these laws of Boyle and Charles were found to be obeyed fairly well by all known gases within the limits of their existence,

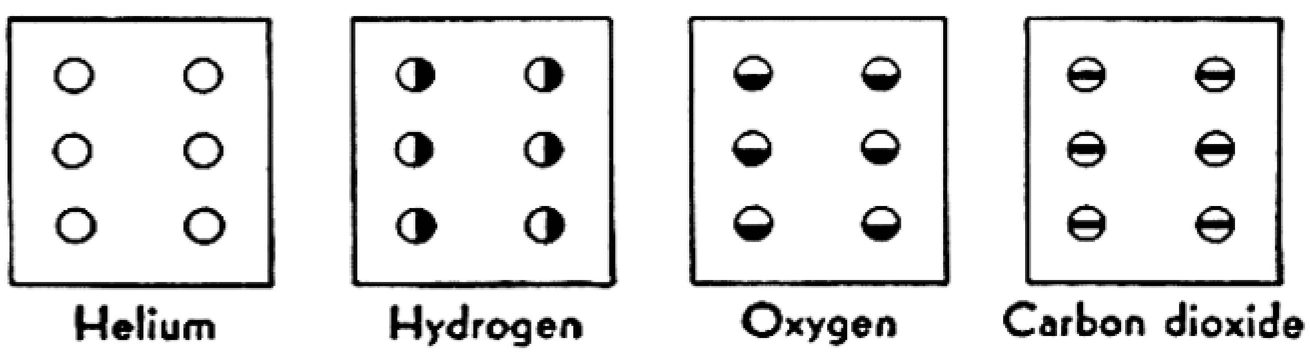


FIG. 27. Avogadro's law—same volume, same temperature, same pressure, same number of molecules.

and since the kinetic-molecular theory appeared to be a suitable explanation of such behavior, Avogadro made what may be regarded as a good guess. It was that *equal volumes of all gases at the same temperature and pressure must contain the same number of molecules.* Since equal volumes of gases under similar conditions of temperature and pressure do actually show the same kinetic effects under heat stimulation, it follows that the kinetic energies of those equal volumes must be the same.

77 Graham's Law of Diffusion

If Avogadro's law is true, the kinetic energy of one molecule of any gas at a certain temperature must be the same as that of one molecule of any other gas; that is, $\frac{1}{2}mv^2$ for one gas $= \frac{1}{2}m_1v_1{}^2$ for another gas. If m is different from m_1 then v must be different from v_1. We shall see later that the mass (m) of one gas must be different from the mass of another gas; therefore the velocities of

gas molecules must vary widely. That this is so was proved by Graham and it can be demonstrated as in Fig. 28. Here a cylinder of porous (unglazed) porcelain is closed by a tightly fitting stopper, through which a tube passes to enter a U tube containing water. To begin with, the cylinder and attached tubes contain air. But when a jar of hydrogen gas is placed over the cylinder, the water in the U tube is pushed down, only to rise on the farther side. This internal pressure means that the hydrogen got into the cylinder faster than the air could pass out. If the hydrogen jar is suddenly removed, the water returns to its position in the U tube and actually shoots beyond that position. This action shows that the hydrogen was in such a hurry to get out that air could not get back in fast enough to prevent a partial vacuum from being formed. Hydrogen is about one-fourteenth as heavy as air; its velocity, therefore, at the same temperature must be greater than that of air if $\frac{1}{2}mv^2$ is to apply to both gases. This behavior is summed up in Graham's law of diffusion: *Under the same conditions of temperature and pressure, the volumes of different gases diffusing through a porous wall in a specified time vary inversely as the square root of the densities.* Thus if sulfur dioxide is 16 times as heavy as helium, it will diffuse more slowly, actually $\sqrt{16}$ or 4 times as slowly.

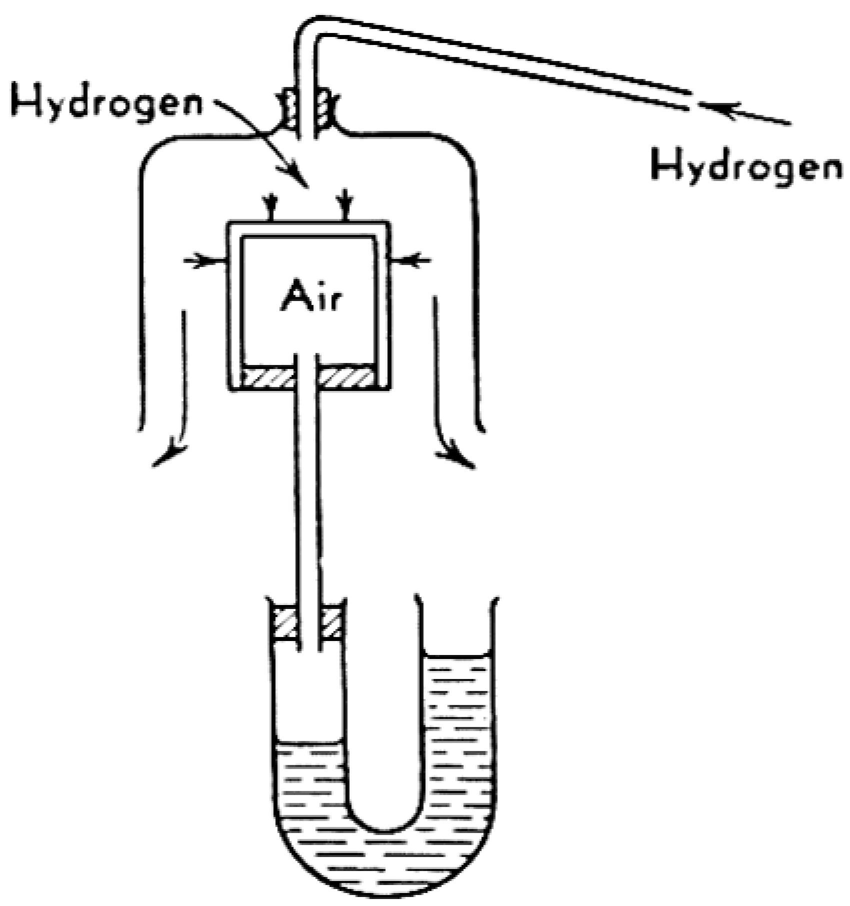


FIG. 28. Hydrogen diffuses through a porous wall faster than air. A pressure is therefore produced inside the porous pot and is transmitted to the water in the U tube.

Gas velocities are actually enormous. Hydrogen, the lightest of all known gases, must have the greatest velocity; the velocity of a hydrogen molecule at room temperature is nearly a mile a second. Calculations from the behavior of gases show that the number of gas molecules in a container holding 22,400 ml at standard temperature and pressure is 61×10^{22}; at that the size of the molecule is such that about 90,000,000, if placed side by side, would extend not farther than one inch. With all these molecules confined in a small space and moving at the rate of, say, a mile a second, it is obvious that many of them are going to collide. It is

possible to calculate just how far one molecule can go before colliding with another under a set of conditions. This distance is called the *mean free path* and increases with decrease of pressure, that is, the molecules get farther apart.

For all the large number of molecules of gas in a given space (such as 61×10^{22} in 22,400 ml), a gas volume under ordinary circumstances is mostly space. A simple example will prove this. If 18 grams (about a tablespoonful) of water is dropped into a completely evacuated container of 22,400 ml capacity (or nearly 5 gallons), it will evaporate and exert a pressure of 1 atmosphere on the walls of the container. Of actual matter present in this large volume, however, less than one-tenth of 1 per cent is actually matter. Yet the gas manages to fill this large space because of its rapid movement. There are times, however, when this small quantity of matter becomes important enough to destroy the validity of the laws of both Boyle and Charles.

78 Deviations from the Gas Laws

In practice when we apply the gas laws we find that they are obeyed perfectly when there are relatively few molecules present in a volume, as when the pressure is very low or the temperature is high or both. But when the pressure becomes high and the temperature low, the proportion of actual molecules to the space occupied becomes significant. Under these circumstances the obedience to the gas laws falls off progressively. Two factors account for this disobedience. First, it was shown by Newton that all particles of matter attract each other in general in direct proportion to their masses and in inverse proportion to the square of their distance apart, $(m \times m_1)/d_2$, where m and m_1 are the masses of two particles and d is the distance separating them. Since d is of the second power and the masses will not alter, it is easily seen how little they attract each other at great distances and how much they attract each other at close range. When this attraction is sufficiently great the free movement of the molecules of gas to travel in straight lines independently of their neighbors is hampered. They therefore tend to come closer together and give a smaller volume than the product $P \times V$ warrants. Second, at sufficiently high pressures and low temperatures the molecules themselves occupy such an important part of the total gas volume and are not compressible that the part of the total volume which

responds to increased pressure is really the space *not* occupied by the molecules. Increased pressure therefore would not in such a case bring about a sufficient decrease in the volume to obey Boyle's law. It would almost seem as if gases obeyed these laws when no gas molecules were present; or as if, in other words, it was empty space that was responding to the application of temperature and pressure. Of course this is not so, but at least it looks that way. The gas laws are said, therefore, to apply perfectly only to the ideal gas.

If a volume of gas is subjected to a sufficiently low temperature and high pressure, the reality of gas molecules becomes apparent; for the gases will change into liquids and here the gas laws will *not* apply. Liquefaction, therefore, is the condition reached when the gas molecules get close enough together and have sufficiently slow motion to adhere together. It is when gases approach the liquefaction point that they tend to disobey the gas laws.

Combining the mathematical expressions of Boyle's and Charles's laws for an ideal gas, we have the expression

$$PV = nRT$$

where P represents the pressure, V the volume, T the absolute temperature, R a constant and n the number of gram molecular weights of gas present.

If the above equation is altered to take care of the deviations previously noted, it reads:

$$\left(P + \frac{a}{V^2}\right)(V - b) = nRT$$

where a is the attraction between the molecules and b is the actual volume of the molecules themselves. However, at ordinary pressures a/V_2 and b may be neglected since they are so small, but they become very important as we approach the liquefaction point.

79 The Liquefaction of Gases

In recent years the liquefaction of gases has become of more than theoretical interest. The reasons for this increased interest are obvious, such as ease of transportation and the use of ammonia, carbon dioxide and sulfur dioxide in refrigeration. Liquefaction represents the utilization of low temperatures and high

pressures in order to reduce the kinetic energy of the gas molecules and decrease their distances apart so that sufficient attraction may result in order to produce the liquid state. Here we are confronted with the differences in boiling point (or liquefaction point) which are characteristic of the different gases. What we have discussed previously on the alteration of the boiling point of water by changes in pressure is applicable to all gases.

One fact, however, has to be taken into account in arranging for the liquefaction of any gas. It is that *each gas possesses some one temperature above which it cannot be liquefied no matter how great a pressure may be applied.* This point of temperature is known as the *critical temperature.* Thus to liquefy oxygen it is necessary to cool it to −118°C anyhow before the application of increased pressure has any effect on its change of state. The pressure required to liquefy a gas at the critical temperature is called the *critical pressure.*

Table 4 shows the boiling points under atmospheric pressure and the critical temperatures of some well-known gases.

TABLE 4

Gas	*Boiling Point, °C*	*Critical Temperature, °C*
Hydrogen	−252.7	−239.9
Nitrogen	−196	−147.1
Oxygen	−183	−118
Carbon dioxide	sublimes	31.35
Ammonia	−33.3	132.4
Sulfur dioxide	−10	157.2
Water	100	374

Some gases, such as chlorine and sulfur dioxide, may be liquefied by cooling with a simple mixture of ice and salt; ammonia and carbon dioxide may be liquefied by liquid air. But eventually we must liquefy air if we wish to use it as a cooling agent for other gases. For this purpose there is a really ingenious device to make a gas liquefy itself. The apparatus for doing this may then be used in general for the liquefaction of all gases no matter how low their critical temperatures may be.

The principle underlying the mechanical liquefaction of a gas is the Joule-Thomson effect. Briefly, it is this. When a gas is compressed work is done on it against the resistance (kinetic

energy) of the gas molecules. The gas thus becomes heated (a bicycle pump gets quite hot during the later stages of filling a tire); conversely, when a gas is forced to expand it cools itself off. If then a gas is compressed into a small space and allowed, or made, to cool down while still under pressure, a sudden release of pressure cools it down still further so that its temperature is lower than at the start. By repetition of this cycle of operations with suitable apparatus the time comes when drops of liquid are produced.

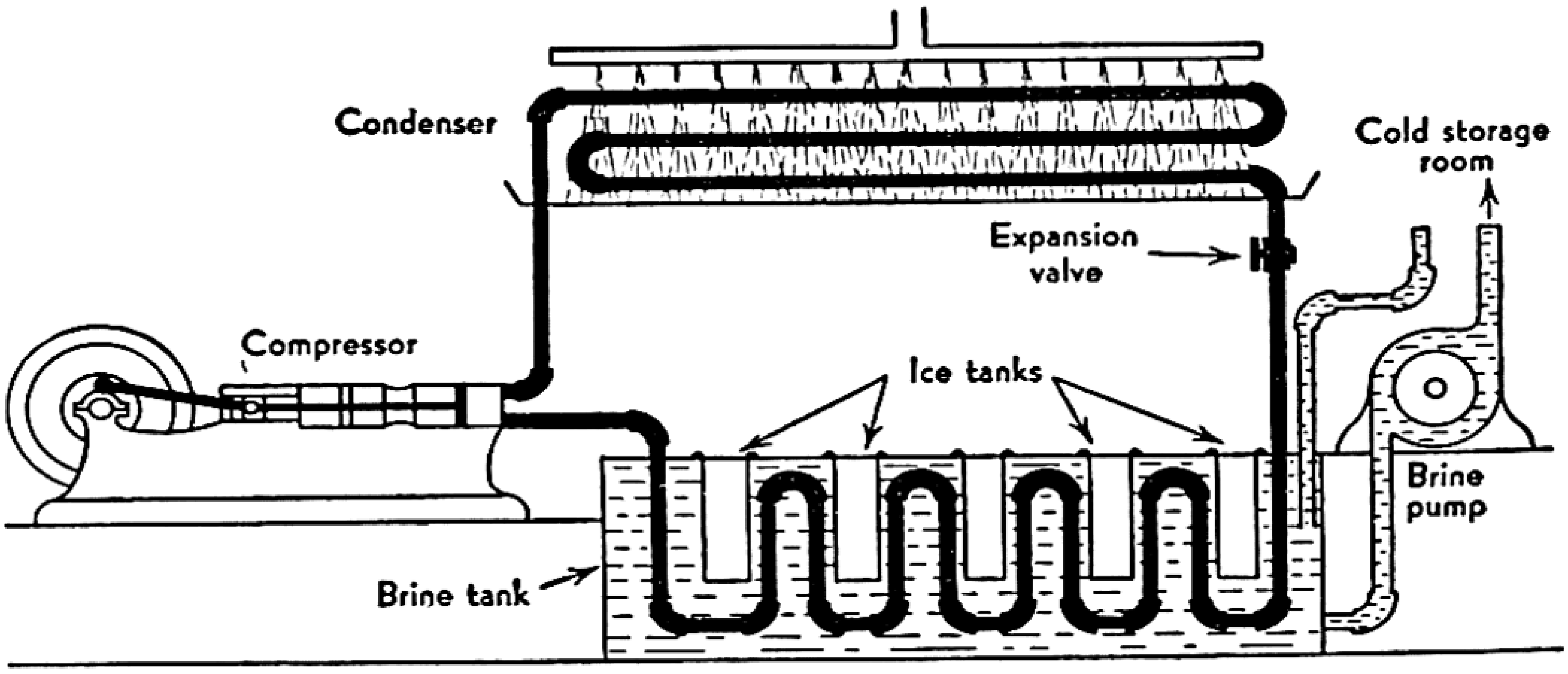


FIG. 29. A refrigerator which utilizes the compression and expansion of gases. Industrial units use ammonia; household units other gases. (Brine is salt water.)

This is especially well demonstrated by the commercial liquefaction of air. (See Fig. 20 on page 51.)

The accompanying diagram of an industrial unit (Fig. 29) illustrates modern methods of refrigeration. One of the newest uses of such units is the highly successful rapid freezing of fruits, vegetables and fish.

80 How to Calculate Gas Volumes and Pressures

1. *Example.* Suppose a volume of gas measuring 370 ml exists at a temperature of 40°C and a pressure of 780 mm mercury. What would be its volume if it were changed to a pressure of 740 mm mercury but the temperature remained the same?

Solution. As long as the temperature remains the same, Boyle's law can be applied. Since the original pressure was 780 mm, the new pressure of 740 mm represents a decrease in pressure and consequently an increase in volume. We therefore multiply the

original volume (370 ml) by a fraction made up of 780 and 740 in such a way that the new volume is larger than the old one. Therefore

$$\text{New volume} = \text{original volume} \times \tfrac{780}{740}$$
$$= 370 \times \tfrac{780}{740}$$
$$= 390 \text{ ml}$$

If the *original* pressure had been 740 mm and the *new* pressure were 780, the fraction would have been $\frac{740}{780}$, since the *new* pressure showed an *increase* over the original and hence the *new* volume must be correspondingly *decreased.*

2. *Example.* If a gasometer with a movable head contains 10,000 cubic feet of coal gas when the atmospheric pressure is 14 pounds per square inch, what will be the volume occupied by the gas when transferred to another gasometer where the external pressure is 56 pounds per square inch, provided that no change in temperature occurs? By the same method of reasoning as in Example 1 above,

$$\text{New volume} = 10{,}000 \times \tfrac{14}{56}$$
$$= 2500 \text{ cubic feet}$$

3. *Example.* What volume of oxygen must be prepared at standard atmospheric pressure in order to fill a steel tank of 220 cubic feet capacity at a pressure of 150 pounds per square inch?

Solution. Since the volume to be calculated is at 14.7 pounds per square inch, a much larger volume is to be anticipated. Hence,

$$\text{Volume required} = 220 \times \frac{150}{14.7}$$
$$= 2245 \text{ cubic feet}$$

4. *Example.* If 50 ml of hydrogen gas at $-23°C$ is raised in temperature to $+27°C$ at a constant pressure, what will be its new volume?

Solution. The first operation to be completed is to change degrees centigrade to degrees absolute by adding 273 to the centigrade temperatures. Thus

$$-23° + 273° = 250°\text{A}$$

and

$$+27° + 273° = 300°\text{A}$$

There is thus an increase in temperature and therefore an increase in volume to be expected. The values 250 and 300 are put into fractional form so as to cause an increase in the value to be obtained. Therefore,

$$\begin{aligned}\text{The new volume} &= \text{original volume} \times \tfrac{300}{250} \\ &= 50 \times \tfrac{300}{250} \\ &= 60 \text{ ml}\end{aligned}$$

If the change in temperature had been from +27°C down to −23°C, the fraction would be $\frac{250}{300}$ since under these circumstances the volume would have decreased.

81 Review of Definitions and Laws

Boyle's law: If the temperature is kept constant, the volume of a given mass of gas varies inversely as the pressure.

Charles's law: If the pressure is kept constant, the volume of a given mass of gas varies directly as the absolute temperature. Or, if the volume is kept constant, the pressure of a given mass of gas varies directly as the absolute temperature.

Avogadro's law: Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

A molecule is the smallest part of an element or compound that can exist free and alone.

The kinetic-molecular theory: All gases are composed of small, separate molecules; these molecules are in a state of rapid motion.

Graham's law of diffusion: Gases diffuse into each other at a rate inversely proportional to the square roots of their densities.

The molecular weight of a substance is a number expressing the relative weight of a molecule compared with the weight of a molecule of hydrogen (2.016).

The gram-molecular weight of a substance is the molecular weight expressed in grams.

The gram-molecular volume is the volume in liters that the gram-molecular weight of a gas occupies at standard temperature and pressure (22.4 liters).

Standard temperature and pressure are 0°C and 760 mm of mercury.

An ideal gas is one which would obey the gas laws at all temperatures and pressures.

The critical temperature of a gas is that point above which it may not be liquefied no matter how great a pressure may be applied.

Absolute zero is the temperature point at which no motion within matter should exist.

82 Summary

The gaseous state of matter is very diffuse and consists of a large number of very small particles operating in a relatively large space. Because of their small mass, small volume and high speed at ordinary temperatures, gases may be compressed regularly by increase in external pressure; they may also assume a larger volume if heat is added to increase the rapidity of molecular motion. Conversely, the molecules may be slowed down by a decrease in temperature. The laws of Boyle and Charles are obeyed by gases (and by gases only) when the temperature is not too low or the pressure too high. This regularity of behavior suggests that the kinetic-molecular theory is correct, and also that equal volumes of all gases at the same temperature and pressure must contain the same number of molecules (Avogadro's law).

A sufficiently low temperature or high pressure, or both, may cause the molecules of a gas to come so close together that, first, they attract each other at short range and, second, they have a real volume that is comparable to the whole volume occupied. They then fail to obey the gas laws perfectly and are preparing to enter the liquid state where the gas laws no longer apply.

Graham's law shows that the movement of a gas molecule is determined by both its mass and its velocity so that K.E. $= \frac{1}{2}mv^2$. Consequently Avogadro's law is dependent upon the fact that at one temperature and pressure the average kinetic energy of all gas molecules is the same.

Questions

1. Using the kinetic-molecular theory explain what occurs during the inflation of a tire by means of a hand pump.
2. A gas measures 100 ml under standard conditions. What will be its volume if the pressure is doubled and the temperature raised to 91°C?
3. A thin rubber balloon is filled with hydrogen and released at the earth's surface. What sequence of changes will occur as it rises? When will it stop rising?
4. What is the relationship among molecular weight, gram-molecular weight, gram-molecular volume?
5. State the laws of Boyle, Charles, Avogadro and Graham.
6. State in your own words what you understand by the following: (*a*) ideal gas; (*b*) critical temperature; (*c*) potential energy as distinct from kinetic energy.
7. Calculate the volume of gas obtained in each of the following cases: (*a*) when 500 ml of oxygen at S.T.P. are subjected to a total pressure of 2280 mm Hg at 0°C; (*b*) when 546 ml of oxygen at 0°C and 580 mm pressure are subjected to a pressure of 1160 mm and heated to 127°C; (*c*) when 2480 ml of nitrogen at 37°C and 745 mm are cooled to −73°C at 800 mm.
8. By means of sketches or in your own words (or both) describe all that will happen when 100 ml of any gas are slowly compressed to the point where liquefaction occurs.

7

Carbon and Life

83 The Life Element

The element carbon is inextricably bound up with the life of this planet all the way from the simplest of plant species to the most highly differentiated of the animals on land, in the sea or in the air. Nor is its importance confined to the present or to the future existence of such forms of life. The organic storehouses of bygone ages provide us with a multitude of creature comforts obtained from coal, petroleum, carbonate and phosphate deposits. Meanwhile the growth and decay of vegetable and animal life continue to utilize carbon in an apparently endless cycle.

84 Carbon in Geological Time

Thus the records of life and of carbon occupy a very important place in geological history. And not only is the record of life as revealed by the study of paleontology and paleobotany one of the most spectacular of geological facts, but the influence of carbon compounds on rock formations has been of such outstanding importance that terrestrial time may be divided into two parts—the pre-Cambrian, when organic carbon was unimportant, and a later and much shorter era when life (and hence organic carbon) was abundant. Table 5 connects the divisions of geological time with the history of carbonaceous matter.

The ultimate source of carbon and, indeed, of all the other elements we know must be sought in the rocks present in the crust of the earth. These rocks are derived from those which were originally molten, the carbon being dissolved in these melts. In some cases compounds of carbon came to the surface and became part of the atmosphere as a result of exhalations from the cooling melt; in others, the melt cooled below the surface, thus entrapping the

TABLE 5

GEOLOGICAL HISTORY OF CARBON

Eras	Periods	History of Carbonaceous Matter
Recent		
Tertiary	(several)	
60,000,000 years ago Mesozoic	Cretaceous Jurassic Triassic	Coal and chalk formation
200,000,000 years ago Paleozoic	Permian Carboniferous Devonian Silurian Ordovician Cambrian	Extensive coal formation First forests First land plants Fresh water fish Development of armored forms of marine animals
500,000,000 years ago Pre-Cambrian	Proterozoic Archeozoic	Development of low plants, and animals without hard parts Atmosphere and hydrosphere formed
Beginning of the Earth 2,000,000,000 years ago		

compounds of carbon, which were able to reach the surface only after prolonged erosion. Part of this carbon was precipitated in the form of carbonates—chiefly limestone ($CaCO_3$)—for limestone beds are found in early pre-Cambrian rock. In its early history carbon was inorganic, but during the long pre-Cambrian era low forms of marine life arose, producing organic compounds in their metabolism. Unfortunately such forms of life have left little record of their achievements.

At the beginning of the Cambrian period there was an abundance of marine life whose records exist because these animals had learned to armor themselves with calcium carbonate, and biogenic deposits

from this time on are found in profusion. At a later date the struggle for existence in the sea became so strenuous that first plants, and then animals, migrated to the land areas. Once the land plants were thoroughly established they became diversified, occupying large areas of the earth's surface. They finally became so abundant that the natural scavenging system broke down and their remains were allowed to accumulate among the beds of rock. Such accumulations of partially decayed and chemically altered material gave rise to what we now call coal. The coal beds in that part of the geological column known as the Carboniferous period are so widespread that much of the coal in Europe and eastern North America is from rocks of that period.

Because of changes in the distribution of land and sea after the Carboniferous period, conditions were rendered unfavorable for coal formation and many feet of rock were laid down over these beds. In later periods other accumulations of coal took place, but such deposits are far less abundant and valuable than those of the Carboniferous era. In general, coal deposits are found in sedimentary rocks which were deposited from fresh water or in marine sedimentary rocks formed near the shore, in which event the vegetation which produced this coal was brought by rivers to the sea.

Coals show such relics of their vegetable origin in their textures as to leave no doubt of their plant origin. Petroleum, on the other hand, shows no such structures, and it is highly probable that it has resulted from the accumulation of the remains of marine animals entombed in the rocks. That carbon deposits like coal remain is evidence of nature's failure to use again immediately the same carbon; and such a large-scale failure may well be an unusual occurrence in her economy. The local accumulation of marine remains may be attributable to some holocaust by which all the organisms were destroyed locally, or it may have been produced in sections of the sea where the normal scavengers could not be supported.

85 Coal and Petroleum

The history of coal or of petroleum begins with the accumulation of biogenic raw material. These beds, forming within the earth's crust, were covered by more and more rock so that the pressure on them became increasingly great, and the rocks con-

taining these remains were pushed downwards into deeper and hotter zones in the crust. The vegetable material became compressed and water was forced out so that, with a continuous operation of this process, complex chemical adjustments resulted in the change of the plant tissue to coal. Because a large part of this change was the loss of hydrogen, the material proceeds from a low-rank coal to one of high carbon content, as exemplified by the nature of lignite and bituminous and anthracite coals. In the animal remains, deformation served to separate out the oil, which,

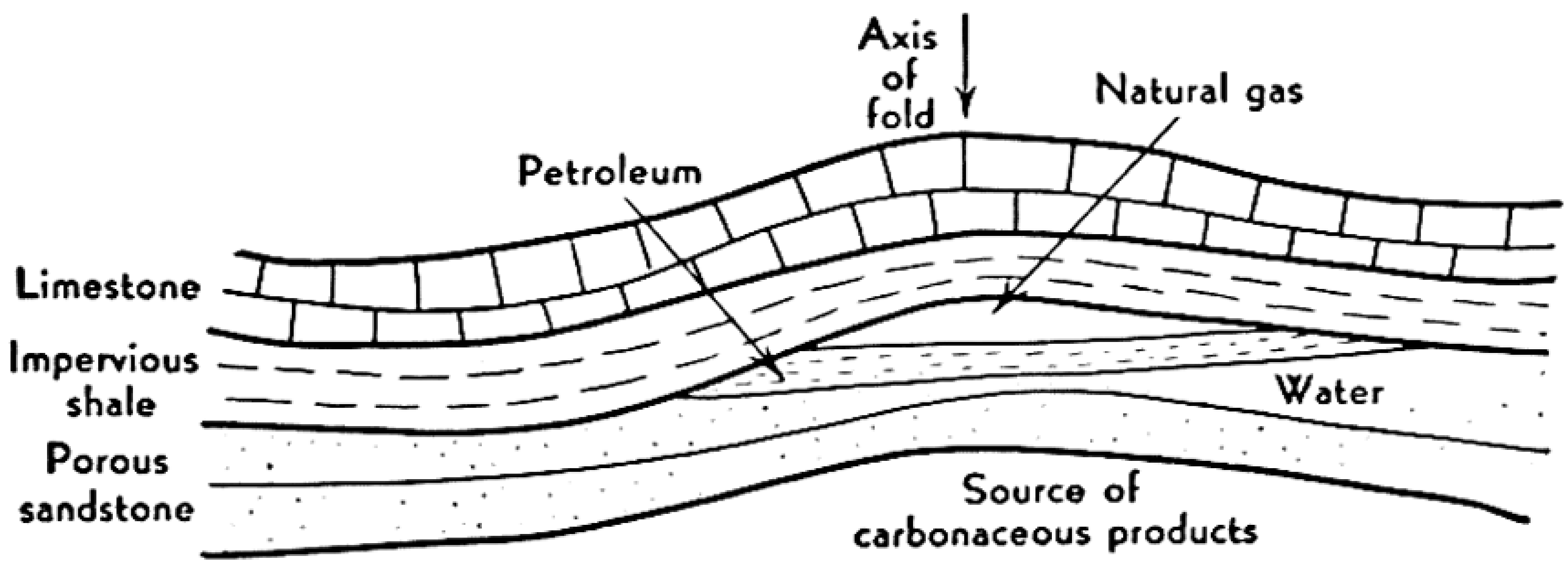


Fig. 30. Vertical section showing accumulation of gas overlying petroleum and water in openings beneath an impermeable bed. The upward warp is an anticline, and a well should be drilled through its crest.

however, is not immune to chemical change. If the restraining pressure is sufficiently low, the oil may be fractionally distilled, the more volatile portions giving rise to natural gas. Coal deposits likewise lose gas but are largely left in their original positions. The oil, however, migrates to pockets under the influence of gravity, tending towards the lowest level of the permeable rocks if water is absent. If water is present, however, the petroleum and natural gas tend to rise to fill openings at higher levels above the water and to accumulate beneath impermeable rocks. Domes or inverted canoe-like rock structures, known as *anticlines*, are particularly favorable for such accumulations.

Because of the changes that have occurred during geological times, coal is not found in old rocks or in those that have been subjected to such treatment as resulted in complete expulsion of hydrogen with the consequent formation of graphite. Oil is found in the less deformed rocks possessing a structure favorable to accumulation, such, for example, as an impermeable cap over beds with pores large enough to permit the free passage of oil, but sufficiently enclosed to retain it. If this covering is broken, gas and

oil escape, the gas entering the atmosphere and the oil being dissipated by streams or inspissated to produce asphalt, as occurred in the asphalt lake in Trinidad or the slime pits of the Israelites.

86 The Fixation of Carbon

Since the beginning of the Cambrian period the fixation of carbon compounds has been to a large extent the result of the activity of living organisms, their shells having formed a large part of the beds of limestone. Coral reefs and the fresh-water marl deposits, being of recent origin, are but feeble representatives of the older ac-

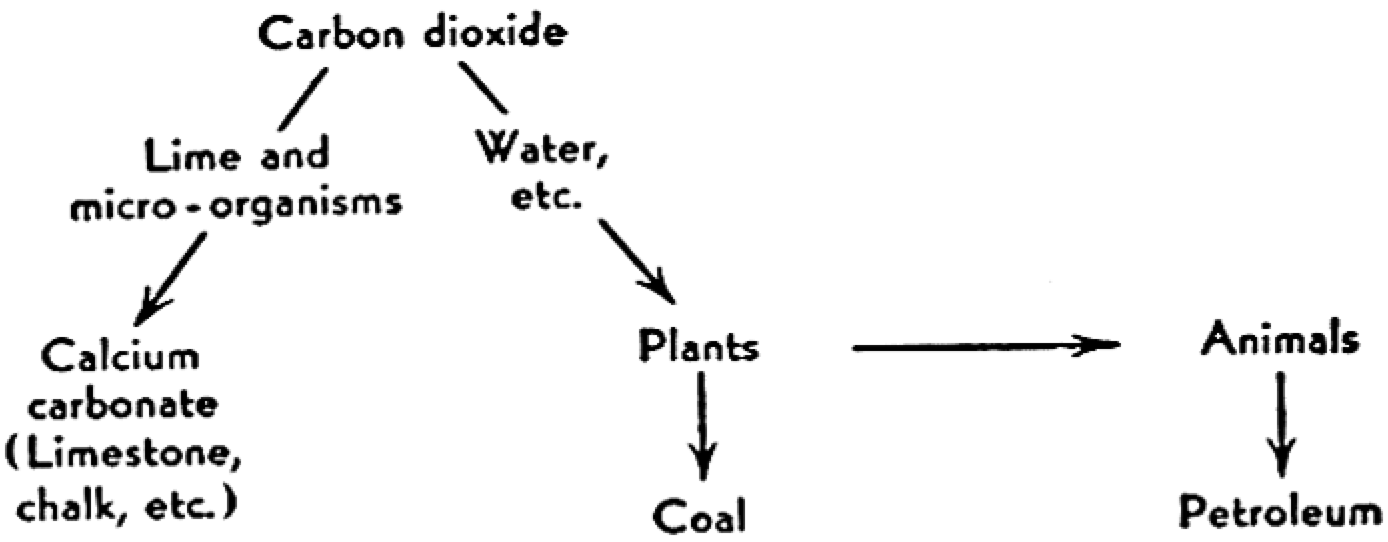


FIG. 31. The biogenic origin of carbonaceous deposits.

cumulations. Coal, petroleum and natural gas, which form such a large part of our industrial economy, represent therefore only the small amount of the carbon in nature's carbon cycle which was trapped in rock as a result of the failure of her scavenging system.

Despite the importance to us of biogenic carbon in later periods, the natural processes which originally contributed carbon dioxide to the atmosphere for the development of living organisms continued to operate for the replenishment of the carbon that had become fixed in rocks. In studying the later geological periods, the geologist is confronted with the problem of whether the carbon has been picked up from the biogenic deposits or is coming to the surface for the first time. For example, a melted rock in contact with buried limestone may, if excess of silica is available, release carbon dioxide according to the scheme:

$$\underset{\text{Limestone}}{CaCO_3} + \underset{\text{Silica}}{SiO_2} \rightarrow \underset{\text{Calcium silicate}}{CaSiO_3} + \underset{\text{Carbon dioxide}}{CO_2} \tag{19}$$

this carbon dioxide rising to the surface and entering the atmosphere to take part in the carbon cycle of nature. Although inorganic nature seems to have made products such as coal, natural

gas, petroleum and asphalt which have proved of great use to humanity, her greatest contribution has been in the provision of carbon dioxide and the elemental forms of carbon, for example, diamond and graphite. Graphite may originate from the drastic heating of coal or petroleum trapped within rock or, in extreme cases, from the reduction of carbon dioxide. Much of the graphite, however, was dissolved in the molten rock and was finally deposited in or near the parent rock by solutions emanating therefrom. Natural graphite has its analogue in the product of the electric furnace.

87 Graphite and Diamond

Graphite is among the softest and least dense of naturally occurring minerals. On the other hand, diamond, also pure carbon, is the hardest natural substance known and is much denser than graphite. It is found under conditions which indicate that considerable pressure was exerted on the melt in which the carbon was entrained. In the process of crystallization the atoms of carbon were packed very close together, so that this very hard and dense form was made. All diamonds found today are believed to have had their origin in certain kinds of rock melts, thus crystallizing under great pressure. Where crystallization proceeded under a lower pressure, graphite was the product.

The uses of graphite depend on its softness, for example, in making the so-called lead pencils and as a lubricant for heavy machinery, whereas the diamond is useful for its hardness, as in cutting, polishing, grinding and boring. The loss of diamonds to industry would be insignificant compared with a cessation in supplies of graphite, for the total production of diamonds for all time is estimated to have reached only sixty-two tons to date.

Such is the history of the geological formation of the key element of terrestrial life. From the various specimens around us a seeming continuity can be demonstrated in vegetable decay, which, beginning with peat (about half carbon), passes into successively purer products, such as bituminous coal and anthracite, to culminate in the pure carbon of the diamond and natural graphite (or plumbago). By the strong heat treatment of coal out of contact with air (*destructive distillation*) a decomposition is induced which drives off various volatile carbon compounds and leaves behind a hard but porous mass known as coke. Except for ash,

coke is nearly pure carbon. A similar treatment under pressure produces a synthetic graphite, also fairly pure carbon, which like natural graphite is an excellent conductor of electricity. The destructive distillation of wood similarly produces a porous but soft product known as wood charcoal, and under the same circumstances animal refuse produces a soft black animal charcoal. If natural gas or oil is burned in an insufficient supply of air, a powder called lampblack is obtained.

88 Allotropy

The capacity of an element for existing in more than one physical form is known as *allotropy*. The various forms mentioned above are allotropic modifications of the same element, carbon. They differ in physical form and other properties but are alike in that they are all insoluble in known reagents and all burn in oxygen to give carbon dioxide. Moissan at the beginning of this century was able to produce small diamonds artificially from sugar charcoal by mixing it with molten iron and suddenly cooling the melt. If a diamond is kept for a long time at a high temperature, it gradually disintegrates, losing its characteristic crystalline structure.

Apart from its great hardness, which is given as 10 in the arbitrary scale of hardness of different solids, the diamond has a remarkably high power of refracting light, the effects of which are enhanced by the method of cutting into faces or facets. Graphite, besides being used as a lubricant when mixed with oil, may be formed into rods which, conducting the electric current, are much used in arc lamps, electrolysis, etc. Wood charcoal is an excellent absorbent of noxious gases, as exemplified by its use in gas masks. Animal charcoal or boneblack can adsorb and retain suspended coloring matter to a high degree and hence is a useful decolorizing agent. Lampblack, when employed as a pigment in paints, has very considerable covering power and is also permanent, being impervious to chemical action under ordinary circumstances. Coke is used largely as a fuel to replace anthracite, but its important application is in the reduction of the oxides of iron in the manufacture of iron and steel (§ 448).

Carbon in all its modifications unites with oxygen to form one or more oxides, with the production of heat and light. At high temperatures carbon combines with hydrogen to form compounds

called hydrocarbons, and with sulfur to form the liquid carbon disulfide (CS_2). Otherwise carbon is resistive to chemical action.

89 Heat from Carbon

Since a large part of our fuels consists mainly of carbon, equations 20–23 are of great significance.

In an atmosphere deficient in oxygen:

$$2C + O_2 \rightarrow 2CO + 58{,}000 \text{ calories} \tag{20}$$

that is, 2416.7 calories per gram of carbon.

But with excess oxygen:

$$C + O_2 \rightarrow CO_2 + 97{,}300 \text{ calories} \tag{21}$$

that is, 8108.3 calories per gram of carbon.

Carbon monoxide burns in air, thus:

$$2CO + O_2 \rightarrow 2CO_2 + 136{,}600 \text{ calories} \tag{22}$$

that is, 5691.6 calories per gram of carbon.

Obviously the more the conditions are arranged to obtain carbon dioxide rather than carbon monoxide, the more heat is produced and the more efficient is the combustion. This fact is of great significance in the burning of coal (largely carbon) and of mixtures of hydrocarbons, as gasoline. Since hydrocarbons (CH_4, C_2H_6, C_3H_8, etc.) are compounds of carbon and hydrogen, the heat of combustion of hydrogen is

$$2H_2 + O_2 \rightarrow 2H_2O + 116{,}800 \text{ calories} \tag{23}$$

that is, 28,968 calories per gram of hydrogen.

This great heat of combustion of hydrogen explains why hydrocarbons may burn to form water and free carbon (soot) since hydrogen enjoys a preferential oxidation. The values given in the above equations are in gram-calories, that is, the weight of the element is in grams and the calorie is the unit of heat in terms of grams of water and degrees centigrade. The British thermal unit (Btu) is the amount of heat required to raise 1 pound (453 grams) of water 1°F ($=\frac{5}{9}$ of 1°C). Therefore 1 Btu = 453 × $\frac{5}{9}$ calories = 252 calories. By using this factor calories may be converted in Btu, the industrial heat unit.

90 Carbon Dioxide

A suitable laboratory method of preparing carbon dioxide is to act upon lumps of marble with 10 per cent hydrochloric acid in a Kipp generator.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow \tag{24}$$

Examination of the properties of carbon dioxide shows it to be colorless and odorless, but with a faintly acid taste. This taste results from its dissolving in the water of the saliva to form the very weak acid, carbonic:

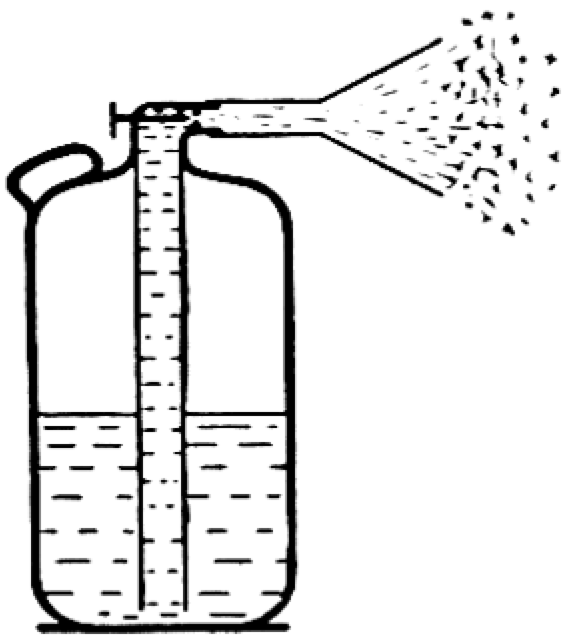


FIG. 32. Compressed carbon dioxide yields "dry ice."

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{25}$$

Carbon dioxide is fairly soluble in water, and its solution under pressure gives rise to soda water, so common in flavored drinks.

When highly compressed and allowed to escape rapidly through a small aperture, carbon dioxide solidifies to a snow-like solid. This solid slowly sublimes, but, if mixed with ether or acetone, a slush is obtained much used as a cooling mixture because of its low temperature, $-79°C$. Blocks of compressed solid carbon dioxide are used for refrigeration purposes under the name of "dry ice."

The affinity of carbon for oxygen at high temperatures is well known in its use as a fuel. Carbon, usually as coke, is largely utilized in reducing metals from their ores:

$$2Fe_2O_3 + 3C \rightarrow 3CO_2 \uparrow + 4Fe \tag{26}$$

This is a simple equation to illustrate a somewhat more complicated reaction. In thus extracting oxygen from a compound, carbon acts as a reducing agent, being itself oxidized in the process to either or both of its oxides CO, CO_2.

If carbon dioxide is passed into limewater (calcium hydroxide), a white precipitate of calcium carbonate settles out:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O \tag{27}$$

If the influx of gas is continued, this precipitate will be seen to

dissolve, a reaction caused by the formation of soluble calcium bicarbonate:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \tag{28}$$

Though the above is a valuable test for carbon dioxide, it also illustrates a reaction in nature of far-reaching proportions. The atmosphere normally contains a small amount of carbon dioxide. This carbon dioxide dissolving in, say, the water of lakes and rivers which frequently flows over limestone beds, brings some of the limestone into solution as calcium bicarbonate. This water, taken up subsequently by animals, is a valuable source of the calcium necessary to the building of the animal skeleton, which contains calcium as the phosphate [$Ca_3(PO_4)_2$].

91 Carbon Monoxide

When carbon dioxide is passed over hot carbon a reaction takes place which produces carbon monoxide:

$$CO_2 + C \rightarrow 2CO \tag{29}$$

Again, the burning of carbon-hydrogen compounds (hydrocarbons) in a supply of air insufficient for the complete conversion of these compounds to water and carbon dioxide gives quantities of carbon monoxide.

Carbon monoxide is a colorless, odorless, tasteless gas, practically insoluble in water. It burns in air—which carbon dioxide does not—with a pale blue flame, producing the dioxide:

$$2CO + O_2 \rightarrow 2CO_2 \tag{30}$$

This reaction may be observed in a coal fire, where carbon dioxide, produced by the combustion of a hot layer of coal, passes over an upper layer of hot coal, producing the monoxide as in equation 30. The monoxide is then seen to burn above the top layer of black coal in bluish, darting flames.

The preparation of carbon monoxide is of great significance at the present time because of two circumstances. First, coal gas may be enriched, for heating purposes, by adding to the gaseous products of coal distillation (§ 465) a mixture of carbon monoxide and hydrogen. This mixture of gases is obtained by passing steam over white-hot carbon:

$$H_2O + C \rightarrow H_2 + CO \tag{31}$$

This hydrogen and carbon monoxide mixture obtained is called water gas and is richer in heat value than ordinary coal gas. Consequently carbon monoxide comes into urban homes in the gas pipes. The second circumstance concerns gasoline, which is used in internal-combustion engines to produce power by its union with the oxygen of the atmosphere. Gasoline is a mixture of hydrocarbons, one of which (heptane) may be taken as an example. Complete combustion of heptane proceeds according to the equation

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \tag{32}$$

In insufficient oxygen, however, the carbon of the heptane may appear as CO_2, CO and C, particularly in warming up a cold engine.

92 Carbon Monoxide, a Poison

Should gases from the household gas pipes or the exhaust of automobiles escape into a small, closed space, a frequently calamitous action of carbon monoxide becomes evident. This gas when inhaled enters the lungs and there combines with the hemoglobin, the red coloring substance of the blood. The compound so formed, carboxyhemoglobin, is difficult to decompose, and in consequence death may ensue. The toxic property of carbon monoxide is evidenced by the fact that inhaling an atmosphere containing 1 per cent of this gas for 10 minutes will prove fatal. A lower percentage naturally requires a longer time of inhalation. But 7 minutes in a small closed garage during warming up may produce insensibility, and 9 minutes death. This poisonous gas is insidious because it lacks both odor and taste. To detect it in gas pipe leaks and in running motor engines in closed buildings calls for constant alertness.

Carbon monoxide is frequently found in coal mines, where its presence was formerly indicated by its effect on canaries, who are very susceptible to it. That it is a component of coal gas may be demonstrated by passing the coal gas through a very dilute solution of blood in water; if the pale red gives place to a definite pink color, carboxyhemoglobin is present. Another test is to allow the gas to come into contact with iodine pentoxide (I_2O_5) in sulfuric acid, its presence being indicated by the mixture's turning green. The poisonous effect of carbon monoxide should never be underestimated.

Carbon dioxide has an interesting use in the treatment to revive those seriously affected by gas poisoning. The oxygen supplied by a pulmotor, as it is called, contains a small percentage of carbon dioxide, which acts as a stimulant to the lungs to increase their absorption of the necessary oxygen.

93 Photosynthesis

By burning any of the commoner forms of carbon in the air or by heating limestone, etc., we may readily prepare the commonest oxide of carbon—the gas carbon dioxide. The importance of this gas cannot be overestimated. It is absorbed by the leaves of plants along with water and, in the presence of sunlight and the chlorophyll (the green coloring matter of plants), is built up into the many chemical compounds that compose all the various parts of a plant, from the root to the ripened fruit. During this process oxygen is given off to the atmosphere; and thus the balance is maintained between carbon dioxide and oxygen, the two gases so vital to the respiration of plants and animals respectively. This process may be summarized thus:

$$\text{Carbon dioxide} + \text{water} \rightarrow \text{plant life} + \text{oxygen}$$

and

$$\text{Oxygen} + \text{animal life} \rightarrow \text{carbon dioxide}$$

94 The Respiration of Plants and Animals

Oxygen and carbon dioxide are of prime importance in sustaining life and promoting growth in nature. Lavoisier showed that plants absorb carbon dioxide and give off oxygen in sunlight; later he was able to prove that the human lungs reverse this procedure, absorbing oxygen and giving off carbon dioxide. The proportion of oxygen in the atmosphere to which animals (and human beings) have become accustomed for many centuries is one-fifth, and if this is changed suddenly a strain is imposed on all who breathe air. Oxygen is used by animals for burning up carbon compounds in the body, providing heat and therefore energy. This oxygen enters the lungs from the air, and the carbon dioxide is largely evolved in the outgoing breath—inspiration and expiration, constituting respiration. Fish, whether in fresh or salt water, depend upon the small percentage of oxygen that is found to a constant degree in all waters exposed to the atmosphere, this oxygen being absorbed through their gills.

95 Natural Reservoirs of Vital Gases

The solubility of oxygen in 100 ml of water at 32°F (0°C) is 4.89 ml; at 86°F (30°C) it is 2.61 ml. Carbon dioxide is much more soluble than oxygen, 100 ml of water dissolving 179.67 ml at 32°F, and 90.14 ml at 68°F (20°C). Since both oxygen and carbon dioxide are found in the atmosphere at all times, it is apparent that the 20 per cent atmospheric content of oxygen loses little to the waters of the earth with their 4 per cent solution. On the other

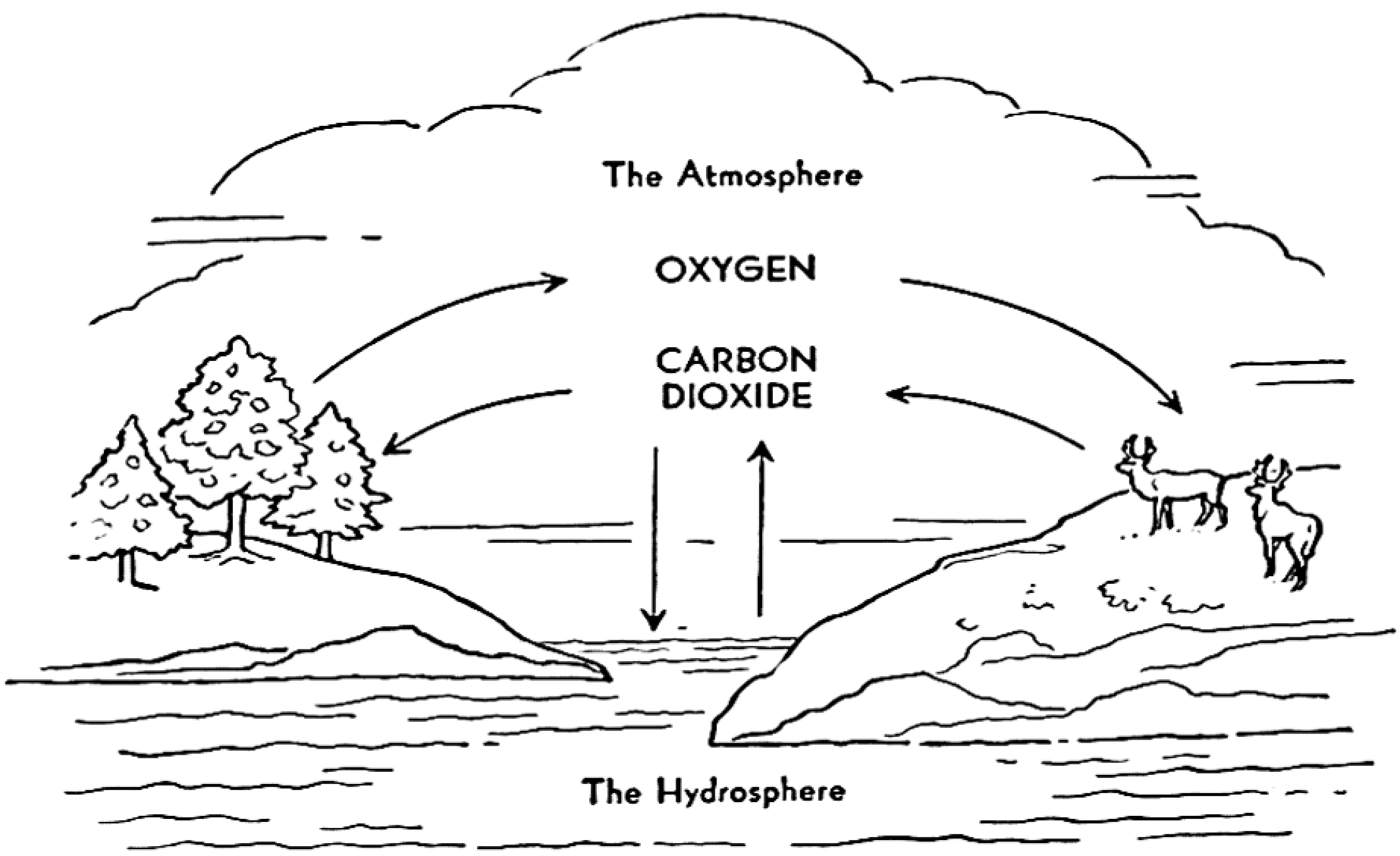


FIG. 33. The atmosphere and hydrosphere act as reservoirs of oxygen and carbon dioxide.

hand, the normal (0.03) percentage of carbon dioxide in the atmosphere is exceeded by the much larger solubility in water. If we allow for the greater volume of the atmosphere by contrast with the hydrosphere, there is a greater universal equality between the two gases than the values for the atmosphere or hydrosphere would suggest if taken singly. In any case it would appear that the atmosphere constitutes the oxygen reservoir, and the hydrosphere plays a similar role for carbon dioxide. Into the atmosphere are poured carbon dioxide from the decomposition of vegetable and animal matter, together with the smaller quantities evolved from coal furnaces, and at the same time the oxygen which is derived from the growth of plants in sunlight. Both these gases may dissolve in the hydrosphere to sustain plant and animal life therein. But the steadying effect of the larger atmosphere and smaller

hydrosphere on the oxygen and carbon dioxide content of both spheres serves to maintain in each sphere the proportions which suit all forms of life, without producing any sudden change that might work to the disadvantage of any living species. (See Fig. 33.)

That this steadying effect does not neglect nitrogen is shown by the fact that, though present in the atmosphere to the extent of 78 per cent, nitrogen is soluble in water to the extent of only 2.35 ml per 100 at 0°C and 1.54 ml per 100 at 20°C. Thus, where nature has given the atmosphere much of one gas and little of another, she has arranged that the smaller hydrosphere is capable of holding little of the first and more of the other. In turn the vast bulk of nitrogen, inert except to the leguminous plants, serves to steady the oxygen and carbon dioxide ratio for the benefit of living matter. That this system of equilibrium works is proved by the constancy of analytical results.

96 The Two Kingdoms

Life on this earth can be classified into vegetable and animal, of which animal is mainly parasitic; that is, plants are self-sustaining and form the food of animals. Some of these animals are plant eaters, like cows and sheep; others, like lions and tigers, are entirely meat eaters and are therefore only indirectly dependent upon plant life. Man subsists by eating both plant and animal tissue and is physically the product of his environment. This environment consists of water, air and salts of calcium, phosphorus, etc. The basic source of human food is the plant kingdom, however, and so man has always been very much concerned with its maintenance.

Prior to the seventeenth century plants were considered to derive all their growth from the soil alone, though there seemed to be no experimental evidence for this theory. About 1600 van Helmont, in an experiment lasting five years, showed that, though a small willow weighing at the start 5 pounds accumulated an additional 159 pounds during that period, only 2 ounces of this weight came from the soil. A number of scientists later, among whom were Mariotte of France and Bonnet of Switzerland, Malpighi of Italy, Priestley of England, Scheele of Sweden and Ingenhousz of Holland, established the following facts: that the ash of plants contains inorganic salts which come from the soil; that plants absorb carbon dioxide from the atmosphere and evolve oxygen when their leaves are illuminated, and reverse this procedure in the

dark; and that water is largely concerned in their growth. The solution of the problem of combustion by Lavoisier established the respiration of plants as a fundamental concomitant of life and growth.

97 Plant Physiology

Thus arose the study of the physiology of plants, that is, the mechanism of the processes whereby they live. Senebier a little later laid emphasis on the importance of sunlight and the green coloring matter found in leaves. But these contributions were mainly provided by chemists, whereas the botanists of the time were concerned chiefly with the discovery and classification of new species. Until relatively recent times, therefore, botany has remained a study of morphology, whereas plant physiology has concerned rather the students of chemistry and physics. Under their leadership a new meaning has been given to the importance of chlorophyll, the green coloring matter of leaves. It is that this substance, or group of substances, under the stimulus of light is responsible for more than mere carbon dioxide and oxygen interchange, for it aids likewise in the production of the vitamins which the human body requires for its maintenance and health.

A simple picture of plant chemistry involves the root, the stem and the leaves. The root absorbs from the moist soil both water and inorganic compounds, such as the chlorides, nitrates and phosphates of ammonia, calcium, potassium and sodium. The stem is strong in proportion to the height and weight of the branches and constitutes a passageway for fluids from top to bottom. The leaves absorb water and carbon dioxide through their stomata (or pores). Certain plants (the legumes) have the additional property of fixing atmospheric nitrogen by means of little protuberances called nodules on their roots.

Though the exact mechanism of formation of starch, cellulose, etc., by the plant is not yet clarified, it is probable that formic acid and formaldehyde are concerned (one or both) in the synthesis from carbonic acid onwards. At least it would appear that for every molecule of carbon dioxide which a plant absorbs one molecule of oxygen is evolved during sunlight.

Such syntheses as plants perform involve the absorption of energy. This energy comes, of course, from the sun and is of really stupendous proportions.

98 The Endless Cycle

The final object of plant life seems to be to propagate its species. To this end the plants produce seeds which consist of the following parts: (1) one or more shells, consisting of cellulose with some inorganic salts; (2) a hard core (when dry) consisting mainly of starch; (3) a small nucleus within this core, containing complex compounds of carbon, hydrogen, oxygen, nitrogen and, to a lesser degree, sulfur and phosphorus. This seed is the latent life which

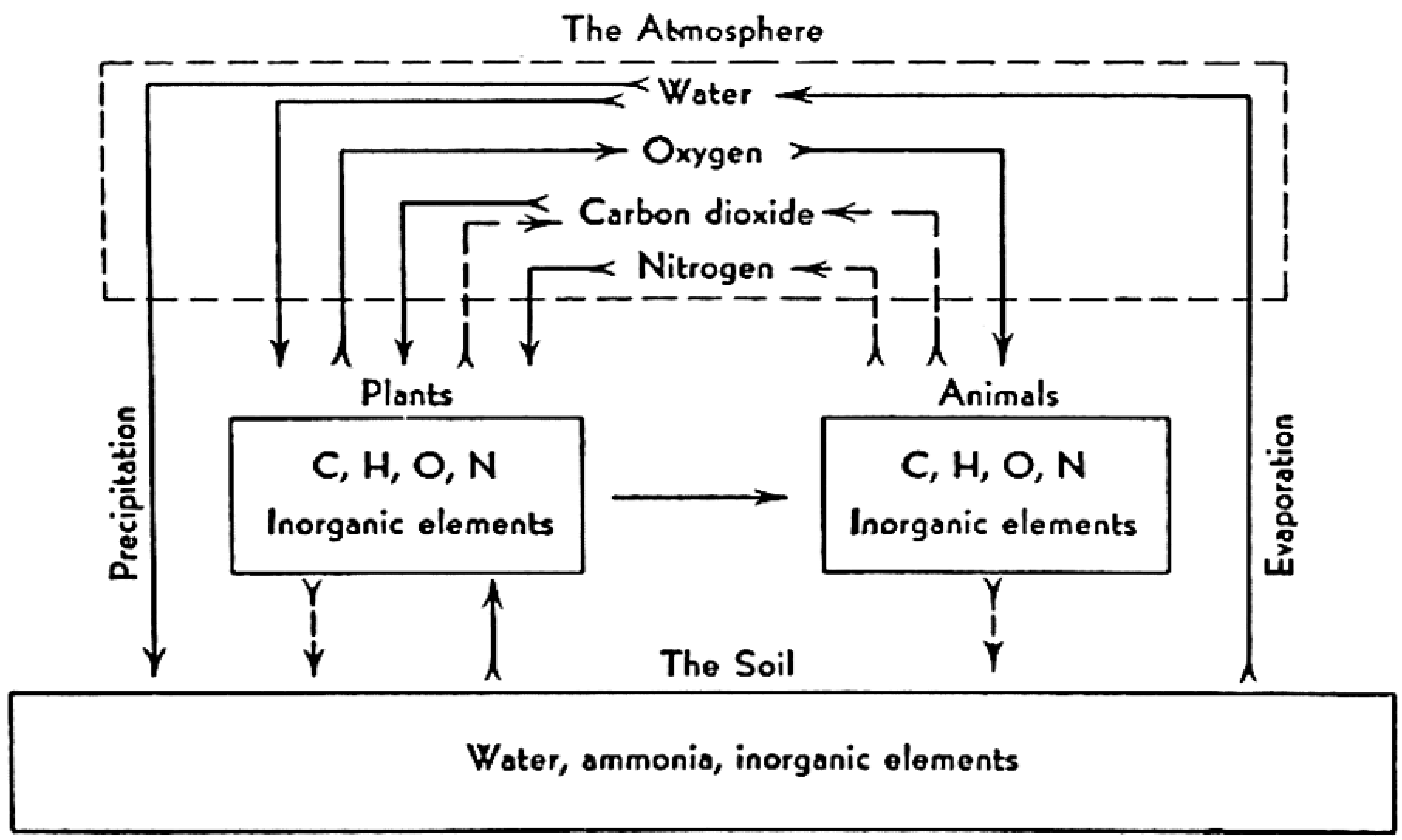


FIG. 34. The cycle of terrestrial life. (Dotted arrows indicate decay.)

grows if planted in warm, moist soil. There it is nursed through its first days by the surrounding core of starch, which decomposes and forms its food until it has a stem, root, leaf and chlorophyll to help it to live by its own efforts, catalyzed by the rays of the sun.

The above life process varies somewhat, of course, with climate and soil conditions. But, on dying, a plant, partially or completely, gives back to the amosphere carbon dioxide, ammonia, etc., these being absorbed either by the atmosphere or by moisture in the soil, or both. Thus the plant returns by its decomposition to the earth which brought it forth. It forms a natural cycle, as shown in Fig. 34; and, since all forms of life are interdependent, this cycle must include both kingdoms.

This cycle shows the air and the soil to be the sources of material to maintain both animal and vegetable life, the air and the sea acting as a reservoir of carbon dioxide and of oxygen. Unfortu-

nately for agriculture—the art and science of plant cultivation—large stretches of land are devoted to growing foods for animals (including man); but these animals on decaying do not in the main give back their inorganic salts to the same soil as produced them. Consequently, the soil becomes gradually denuded of these inorganic salts. They must be replaced by artificial fertilizers, which are unnecessary in the jungle, for example, where plants die and give back to the soil, by means of nature's own scavenging system, all the inorganic salts they took out of it; but they are very necessary where large tracts of land are under cultivation. It is thus evident how man has upset the natural balance and must pay for it —sometimes in floods, sometimes in soil drift.

A complete replacement of nitrogen compounds is not essential, since bacteria (minute animal organisms) as well as the leguminous plants fix the atmospheric nitrogen, forming soluble compounds which are washed by rain or dew into the soil. Frequently land goes acid and requires lime. Indeed, different crops require different soil conditions, and the modern artificial fertilizer is an attempt to supply the required ingredients. These fertilizers usually contain ammonium sulfate, sodium nitrate, potassium chloride and a phosphate. A natural source of phosphate is calcium phosphate, which when treated with sulfuric acid produces a mixture of calcium acid phosphate and calcium sulfate (hydrated), soluble in water and known as superphosphate. By such means are the lost ingredients replaced in the soil.

99 Summary

All living matter is composed of carbon, and the deposits of the Paleozoic and Mesozoic eras are the result of life. Plant life is responsible for our coal deposits whereas natural gas and petroleum were produced from animal life. Calcium carbonate, as limestone, chalk and coral, is the accumulation of microorganisms similar to those which produce coral today.

The element carbon illustrates the phenomenon of allotropy—the ability of an element to exist in more than one physical form. Diamond and graphite are two crystalline forms of carbon.

All forms of carbon unite with oxygen to produce oxides. In an excess of oxygen carbon burns freely to carbon dioxide (CO_2), but in insufficient oxygen the lower oxide, carbon monoxide (CO), is produced. Carbon and some of its compounds—gas, coal and petroleum—are the main source of heat and power.

Carbon dioxide is prepared by two general methods: by burning carbon of some form in an excess of air or oxygen and by decomposing a carbonate. The

combustion of carbon to produce carbon dioxide evolves heat and is the chief industrial source of heat energy.

The decomposition of carbonates is represented in the laboratory by treating limestone ($CaCO_3$ or calcium carbonate) with an acid. Industrially, carbonates are decomposed by heat, as in making lime (CaO) from limestone, when carbon dioxide is given off.

Solid carbon dioxide is used on a large scale as a refrigerant and as a fire extinguisher; on subliming it leaves no liquid or solid residue.

Carbon monoxide is formed when carbon and its compounds (for example, coal and gasoline) are burned in insufficient oxygen.

Carbon monoxide is very poisonous because it forms with the hemoglobin of the blood a compound very difficult to decompose. This gas has been the cause of many fatalities in coal mines.

Carbon dioxide and oxygen are essential to plant and to animal life, respectively. Plants in sunlight absorb carbon dioxide and give out oxygen; this oxygen is absorbed by animals who give out carbon dioxide in their turn.

Both the atmosphere and the hydrosphere cooperate to maintain the constancy of supply of oxygen and carbon dioxide for the biosphere.

Nitrogen and phosphorus are obtained chiefly from their compounds in the soil, but some plants can fix atmospheric nitrogen by themselves. Materials known as fertilizers are often added to the soil to replace these inorganic elements.

Nature presents a cycle of carbon and nitrogen. As these elements are absorbed by growth, so they are given back on death to be used over again. Nature is both lavish and economical.

Questions

1. Trace the formation of limestone, coal and petroleum through geological time.
2. Nature does not waste matter. What evidence have you for this statement?
3. Compare the properties of diamond, graphite, charcoal and lampblack. What property do these forms illustrate?
4. Of what importance is carbon dioxide in life processes?
5. Of what sources of heat can you think which are not associated with carbon?
6. How may carbon dioxide be prepared?
7. Compare the physical and chemical properties of carbon monoxide and carbon dioxide.
8. To what is the toxicity of carbon monoxide due?
9. By what tests may the two oxides of carbon be detected?
10. Explain the presence of the deposit found in kettles in which water from a limestone region is boiled.
11. Outline the utilization of oxygen and carbon dioxide in natural occurrences.
12. What is photosynthesis?

8

Chemical Longhand and Shorthand

100 Chemical Longhand

The previous chapters have presented the reader with a few of the more important substances in chemistry, and names have been given to them in what may be considered a very arbitrary or haphazard manner. Likewise it has been stressed that some words in common use have a restricted meaning in the vocabulary of the chemist. It will shortly become apparent that the chemist has been obliged further to resort to the use of abbreviations, which are nothing more or less than a highly developed system of shorthand.

101 Evolution of the Element

So far, consideration has been given to quantities of matter without regard to the details of their finer composition, though composition was the subject of much non-experimental speculation by the ancient Greeks. They conceived all matter to be constituted of some one simple substance, which, by some curious and inexplicable variation, would give the characteristics associated with such different bodies as air, water, stone, or wood. Thus in succession were postulated the four primal elements, earth, air, fire and water; but how these actually made up what we call matter they never satisfactorily explained. The first suggestion of value in this respect seems to have come from the Hindu philosopher Kanada, who said that matter is discontinuous, or composed of tiny separate parts later called atoms. Thus, it was thought, all kinds of matter are composed of their smallest parts, the atoms of each kind in close proximity but separated by an all-pervading fluid, the hypothetical ether.

It was really not before the eighteenth century that the discovery of a few of what we now call the chemical elements revived

and emphasized the importance of the atomic idea. During this period the practical separation from one another of such elements as hydrogen, oxygen and nitrogen led to the discovery of certain regularities which appeared only when quantities of these elements were made to combine and form compounds.

102 Synthesis and Decomposition

When a substance on analysis can be shown to be composed of only one kind of matter it is called elementary or an *element*. Elements are therefore the simplest constituents of matter, and it is from them that the intricate structure known as matter has been built. Although in the construction of a city the actual building materials may be very few in kind—wood, stone, steel and bricks—it is possible by varying the proportion and arrangement of each to erect a multitude of edifices no two of which are exactly alike in appearance, design or use. So it is with chemical compounds. Inevitably certain general principles of construction must be followed; in this chemistry differs from no other art or science. Also, in the demolition of a building whose parts may be used again, the wrecking gang will sort out the various pieces. Then they will see what kinds and proportions of materials the building was composed of, although it has now lost its symmetry and is but a heap of ruins. So from elements such as gold, silver, copper, lead, oxygen, hydrogen and nitrogen, chemical compounds may be built up by a process which we call *synthesis*, and these compounds may in turn be taken to pieces or *decomposed* again into its elements.

103 Cementing Atoms

Of course in any building there must be at least one means of holding the various parts together, such as nails or bolts or cement. Just so elements were thought to become attached to one another by some sort of mutual attraction which we still refer to as *chemical affinity*, especially when we are unable either to define the attraction exactly or to resolve it into all its factors. Recently it has come to be realized more and more that electrical forces play an enormous part in this cementing of elements. Obviously, too, it requires force to undo this cementation in proportion to the adhesive nature of the cementing forces. Without committing ourselves at the moment to a complete explanation of what con-

stitutes this adhesive or cohesive force, we are able to determine to what extent it exists between, say, a pair of elements and how it may vary in quantity. This holding force we interpret in terms of a unit, which we call *valence.*

It is quite apparent that if a piece of, say, iron is cut in two, and if one of these halves is further halved and so on, this process can theoretically go on *ad infinitum* without the actual destruction of the iron. Which small part is the atom? Scientists of the early nineteenth century arbitrarily stopped short by considering an atom to be that smallest part which could enter into combination with some other atom to form a compound; whereas the smallest part of a compound that could exist free and alone was called a molecule. This conception of the atom has been, and still is, extremely useful in making possible the visualization of what occurs during an interchange of position of atoms, that is, a chemical reaction.

104 Chemical Shorthand

At first these atoms were thought of as tiny spheres, and their union one with another was thought to be by means of hooks. This simplification of representation leads to a system of shorthand for chemistry. An atom of any element was represented originally in a more complex manner than now. The simple system now in use is due partly to Lavoisier and partly to the Swedish chemist Berzelius.

105 Symbols

This system indicates each of the elements by a capital letter, usually the first letter of the name, for example, carbon, C; fluorine. F; oxygen, O; hydrogen, H. If the one letter is found inconvenient, the first letter (written as a capital) and one other (written small) in the name are chosen; for example, chlorine, Cl, since C is taken for carbon; or one or more of the letters of the Latin name of the element, as K (kalium) for potassium since P is kept for phosphorus; Ag for silver (argentum), A being kept for argon; Hg for mercury (hydrargyrum).

Where confusion might result, as in elements with the same first letter and no Latin equivalent, the first letter and some significant letter from the body of each name were chosen, for example, magnesium, Mg, manganese, Mn, molybdenum, Mo. The short-

hand letters are called *chemical symbols*, and, when found standing alone, they represent not merely the element itself but one atom of that element as well.

106 Formulae

When we wish to write a chemical compound in shorthand, we put down, side by side, the symbols of the elements found in that compound. Thus HgO refers to a compound of mercury and oxygen, called mercuric oxide. But a formula does more than this. HgO implies that this one molecule of mercuric oxide contains *one* atom of the metal mercury joined chemically with *one* atom of the gas oxygen, that is, a formula tells not merely of what kind of elements a compound is made up but also in what proportion—in other words, its chemical composition. Thus $KClO_3$ indicates a molecule of potassium chlorate and also states that this molecule contains the metal potassium, the greenish-yellow gas chlorine and the colorless gas oxygen in the atomic ratio of 1:1:3.

107 Atomic Weights

But before a collection of symbols could be put together in a formula to represent the molecule of a compound, it was necessary to know how many atoms of each element were involved. This knowledge required an exact analysis of each such compound, and this analysis in turn demanded a system of quantities. Because it was obviously impossible to isolate a single atom of each element and weigh it, a system was devised to represent the weights of the atoms. This system is treated more extensively in a later chapter. In essence, however, it amounts to this: Equal volumes of various elements are known to have different weights, and of all the elements hydrogen is the lightest. If, therefore, an equal number of, say, hydrogen, oxygen and nitrogen atoms can be got together and weighed, the relative weights of oxygen and nitrogen atoms in terms of hydrogen can be obtained. This system proved successful in demonstrating that the atom of oxygen must be 16 times as heavy as that of hydrogen, nitrogen 14 times, etc. It is known as the atomic weight system, where, hydrogen being arbitrarily taken as 1 (actually 1.008, to be exact), oxygen becomes 16, nitrogen 14, etc. This does not mean that an atom of hydrogen weighs 1 gram or 1 pound or 1 ton, but it does mean that the number of atoms of hydrogen weighing 1 gram will be the same as the

number of oxygen atoms which weigh 16 grams, and 14 grams of nitrogen will contain that same number of atoms.

108 Laws of Chemical Union

With this system, which took many years to develop, the composition of compounds became intelligible. For example, 18 grams of water can be decomposed into 2 grams of hydrogen and 16 grams of oxygen; this suggests that the molecule of water must be composed of two atoms of hydrogen and one atom of oxygen. This 18, called the *molecular weight* of water, is the sum of the atomic weights of the atoms composing the water molecule. The composition of water by weight can be verified wherever a sample of pure water can be obtained and analyzed. Furthermore, 2 grams of hydrogen and 16 grams of oxygen will always give rise to 18 grams of water when they are combined—always just so much, no more, no less.

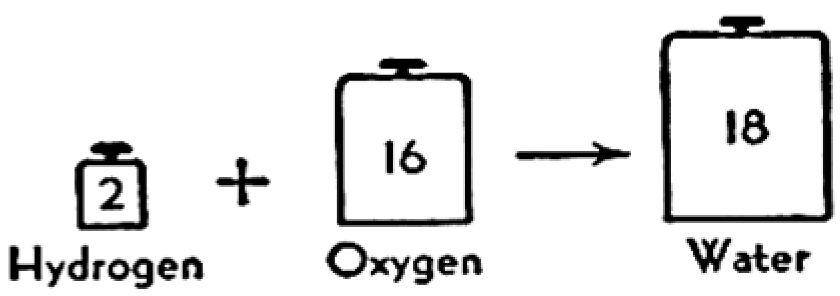


FIG. 35. The constancy of mass in chemical union.

This fact, as well as the results of many similar experiments, led to the formulation of what are now regarded as laws.

(1) When elements combine to form a compound they always do so in fixed proportions by weight—the *law of definite proportions,* or law of constant composition. Thus the formula HgO means that mercuric oxide contains the elements mercury and oxygen always in the fixed proportion of 200.6 to 16 parts by weight. That this is true experimentally is confirmation of the idea that the atom is chemically indivisible, and that compounds are formed by the union of these small entities called atoms whose existence was at first only assumed.

(2) When elements combine to form compounds they do so in simple ratios of their atoms, and hence of their atomic weights. So CO_2, which is actually C_1O_2 (we never write 1, any more than we do in algebra), and not $C_{90}O_{180}$. The statement given above is known as the *law of combining proportions.*

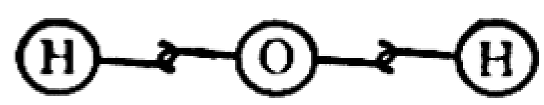
(3) When elements combine to form a compound, or when a compound is decomposed into its elements, there is no loss or gain in total weight—a simple way of stating the *law of conservation of mass.* There is nothing complicated in this statement of a very

fundamental truth, that we are unable to create or destroy matter. If we could accomplish either, there would be no order in nature, merely chaos. Concretely this law states for the chemist that 18 grams of water must always contain exactly 2 grams of hydrogen and 16 grams of oxygen, must yield exactly these quantities on decomposition, and that these separate quantities of the two elements cannot on recombination give rise to more or less than 18 grams of water. And so it is with other quantities of matter involving chemical changes. It is this quantitative side which makes chemistry an exact science, since it is based on strict though simple mathematical relationships.

109 Hooking up the Atoms

Given these ideas of integral relationships among the elements and their atoms, we are now ready to consider the earliest rational method of visualizing chemical combination. Representing the atoms of hydrogen and oxygen by spheres we have H O; the molecule of water must contain two such hydrogen spheres to each single oxygen sphere. Using the old hook idea of attaching the atoms, we have two hydrogen spheres, each with one hook; for these to be attached to the oxygen requires that the oxygen spheres possess two hooks, thus

Water then becomes



Later the hooks became simplified, and the idea of solid spheres is discarded, so that the formulation of the union of hydrogen and oxygen became:

H— and —O— and —H unite to form H—O—H

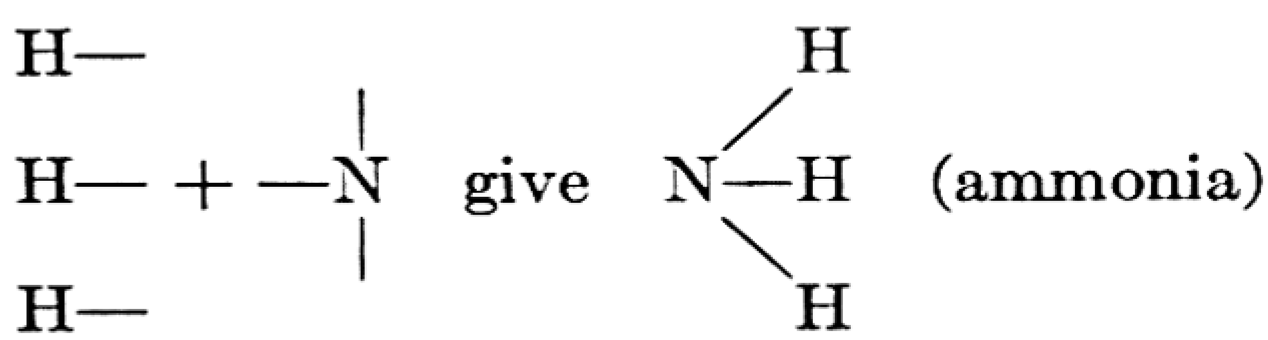
Each — attached to the symbol for the element became known as a bond. It must be remembered that these hooks, and later bonds, were merely a visual method of representing that elements were capable through their atoms of linking up with other elements to form compounds. It may have been a very artificial method but it has been, and still is, very useful.

110 Valence

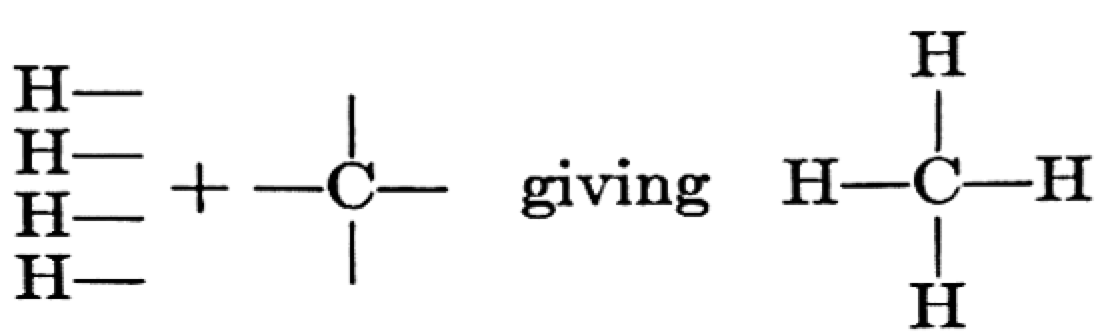
With this simple system of linkage, a system of atomic weights and the ability to analyze a great variety of chemical substances, chemists were unable to find a single compound in which one atom of hydrogen appeared to be combined with more than one atom of another element. The atom of hydrogen was therefore left with a single bond. To account for the composition of compounds, the atoms of many other elements had to be represented as having more than one bond, as the oxygen above. Ammonia gas represented another stage in this linkage scheme, for 17 grams of ammonia are made up of 3 grams of hydrogen and 14 grams of nitrogen, that is, the molecule of ammonia consists of 3 atoms of hydrogen and 1 atom of nitrogen.

To represent this graphically required showing the nitrogen atom with 3 bonds, one for each of the 3 hydrogens.

Thus



So the number of these bonds possessed by any atom became known as the holding power or *valence* of the element concerned. The gas methane may be analyzed into 12 grams of carbon and 4 grams of hydrogen for each 16 grams, and the linkage of the atoms is shown thus:



Here the carbon atom is shown with 4 bonds. Thus arose the valence system, showing hydrogen as monovalent, oxygen divalent, nitrogen trivalent, carbon tetravalent, etc. The representation of chemical formulae apparently becomes similar to the fitting together of pieces in a jigsaw puzzle. For example, how can the formula of carbon dioxide be guessed at by this means? If there are 4 bonds on a carbon atom and 2 on an oxygen atom, the simplest picture showing no free or unattached bonds may be arrived at as

follows, where the plus sign has its algebraical significance of "added to":

$$=\!C\!= + \; O\!= + \; O\!= \quad \text{give} \quad O\!=\!C\!=\!O$$

This picture suits the name carbon dioxide, 2 atoms of oxygen to 1 atom of carbon. That this formula is correct may be checked (from the atomic weights), since 44 grams of carbon dioxide are composed of 12 grams of carbon and 32 (that is, 2×16) grams of oxygen.

111 Graphical and Empirical Formulae

This graphical method of representing compounds is used now only when the mode of linkage of the various atoms in a compound requires demonstrating. It is now more usual to employ the simpler H_2O, NH_3, CO_2, etc., these simplified statements of composition being known as *empirical formulae.* When symbols and formulae are put together to represent a known chemical reaction, they are called equations, since there is an equality of mass before and after such a reaction (law of conservation of mass).

112 The Pairing of Atoms

For experimental reasons it has been found necessary to represent both compounds and elements in such a way (especially when they are gases) that no free bonds are apparent in a molecule. We might expect this from seeing the representation of a hydrogen atom (H—) or an oxygen atom (—O—). Such bonds to the chemist represent a known fact, namely, that atoms can seldom be found existing alone. What more natural than that they join up with each other? Thus

$$H\!- + \; H\!- \quad \text{might become} \quad H\!-\!H, \text{ or } H_2$$

and

$$O\!= + \; O\!= \quad \rightarrow \quad O\!=\!O, \text{ or } O_2$$

Actually a consideration of the weights and volumes of hydrogen and oxygen which combine to form water renders it absolutely necessary that the molecule of these gases (as of most other gaseous elements) be so written, or in the simpler empirical manner, H_2, O_2. That is what is implied in the general statement that *there are usually two atoms in the molecule of an elementary gas.* The symbol H has the following significance: (1) the element hydrogen, (2) an

atom of that element as it may be conceived of as taking part in some chemical reaction and (3) 1 gram of hydrogen; whereas H_2 signifies (1) the element hydrogen existing alone as a double atom (a *molecule*) and (2) 2 grams of hydrogen. Analogous statements may be made about O and O_2, N and N_2, Cl and Cl_2, etc., but an exception must be made as far as the rare gases are concerned (see § 129).

113 Chemical Equations

Examples of reactions met in earlier chapters may now be formulated into the chemist's equations:

$$2H_2 + O_2 \rightarrow 2H_2O + \text{energy} \tag{33}$$

(*a*) Hydrogen gas and oxygen gas unite to form water and liberate energy.
(*b*) Two molecules of hydrogen will react with 1 molecule of oxygen to give 2 molecules of water.
(*c*) Four grams of hydrogen and 32 grams of oxygen unite to produce 36 grams of water.
(*d*) And, as was seen in the experiment on the electrolysis of water, 2 volumes of hydrogen and 1 volume of oxygen will unite to form water (really to form 2 volumes of water, if water is measured in the gaseous state).

$$C + O_2 \rightarrow CO_2 + \text{energy} \tag{34}$$

(*a*) Carbon and oxygen unite to form carbon dioxide and liberate energy.
(*b*) One atom of carbon unites with 1 molecule of oxygen (= 2 atoms) to form 1 molecule of carbon dioxide.
(*c*) Twelve grams of carbon unite with 32 grams of oxygen to form 44 grams of carbon dioxide.

Since carbon is a solid and not a gas, the complexity of its molecule is now known, and so it is represented merely by its symbol as if it existed free as atoms.

The above examples serve to show how systems have been built up during the last century and a half to collect into one simple system all the important ideas developed from the study of chemical experiments. To the reader who does not intend to pursue further study in chemistry, symbols, formulae and equations are

not of great interest or value; they do, however, tend to demonstrate how facts may be made to interlock with ideas to produce a useful and, at the same time, an accurate system. It is only to be expected that the old systems of hooks and bonds may be criticized on the ground that they do not tell what forces are causing substances to combine or how these forces really act. It is freely admitted that such criticism is in order, but not justifiable in the light of the fact that the actual composition of the atom itself drew attention to itself only at the beginning of this century. Indeed it is only within the last thirty years that such study has been of use to the chemist. In this time it has in great measure, as will appear later, tended to render graphical formulae more than ever applicable to the solution of problems rather than devoid of meaning. That the system of bonds has been of inestimable value may be inferred from the fact that it is still in daily use after three quarters of a century. It conveyed to the early organic chemist a visual representation of the constitution of complex carbon compounds long before any of the brilliant but relatively recent researches into the make-up of the atom began to demonstrate the electrical nature of chemical combination.

114 Review of Definitions

Synthesis is the building up of a chemical compound from simpler parts, either elements or compounds. It is thus the antithesis of decomposition.

A symbol is a shorthand method of indicating an element; it may be a single letter or, in many instances, two letters derived from the name of the element concerned.

A formula is a collection of two or more symbols placed close together; it indicates what elements are joined in a particular compound and also the proportions of such elements.

The atomic weight of an element is a number expressing the relative weight of an atom of that element compared with the weight of an atom of hydrogen (1.008).

Valence is the ability of an atom of an element to hold in combination a number of atoms of hydrogen. It is expressed by some number ranging from 0 to 8, inclusive.

The law of definite proportions (or law of constant composition) states that when elements combine to form a certain compound they always do so in the same proportions by weight.

The law of combining proportions states that when elements form compounds the proportions by weight of the elements are simple ones.

An equation is a collection of symbols and formulae to indicate what substances are reacting and what substances are formed by a reaction. It goes

further and states how much of each is concerned, so that the total mass of the products of the reaction is equal to the total mass of the reacting substances at the start.

115 Summary

The term element has evolved from an indefinite conception of the simpler components of matter to become a substance which cannot, by chemical means, be subdivided to give two or more still simpler and different substances.

Compounds are formed from the atoms of elements by means of some inherent attractive forces operating between such elements. These attractive forces tend to hold the atoms together in the compound against such disruptive forces as the external application of energy.

These attractive forces cause elements to link themselves together in a regular manner, first as regards number of atoms and second as regards the masses of these atoms. This regularity makes possible the statement of the laws of definite proportions and of combining proportions. Furthermore, this regularity can be stated in terms of number of atoms for each different kind of element and with reference to the lightest of all elements, which is hydrogen. The summation of combining regularity is expressible in the term valence.

The atoms of elementary substances tend to go together in pairs.

Questions

1. How do hydrogen and oxygen differ from the elements of the Greek philosophers?
2. Compare synthesis with decomposition.
3. Can you visualize an atom?
4. Elements unite to form compounds. Can you show this pictorially?
5. State and illustrate the laws of chemical union.
6. Illustrate the use of valence links.
7. Show how symbols make up formulae and how both may be involved in the making of an equation.
8. What is the mass significance of an equation?
9. Define valence in your own words.
10. Since oxygen has a valence of two, write the formulae graphically for SO_2 and SO_3. What valence will you assign to sulfur in each case?
11. Given the valences calcium = 2, oxygen = 2, chlorine = 1, aluminum = 3, write the formulae for calcium chloride, aluminum chloride, calcium oxide.
12. Supposing that the valence of an element were caused by certain available quantities of electricity in each element, what would you conclude as to these quantities?
13. Review equations 1 to 32 from page 42 to 84 in the following ways: (*a*) write down each equation; (*b*) name each element or compound shown; (*c*) tell in your own words what each equation means.

9

A Chemical Family—the Halogens

116 Family Life among the Elements

So far very few of the elements have been mentioned and then under circumstances which involved contrasts rather than similarities. But now our attention is to be given to a group of four elements, fluorine, chlorine, bromine and iodine, the symbols of which are F, Cl, Br and I, respectively. In a classification of the elements on page 197 these four appear in the vertical column, or *group* as it is more commonly called, that is headed by the numeral VII. This is not an arbitrary classification, as we shall see later (Chapter 17), but one based on the very constitution of the atoms themselves. Each of these groups contains elements which show a striking resemblance to each other. This group of four elements happens to be of great chemical interest and, in addition, serves the purpose of demonstrating that all the groups of this classification are merely families containing members which resemble one another, and yet differ somewhat, just as do the members of any human family. Always excepting the first member, which is in a somewhat different relationship, they show striking similarities in appearance and behavior. As a rule, the similarities displayed by a group show a graded relationship from top to bottom, and this is particularly so with the halogens.

All four elements have long been known as the halogens (salt-formers) because of the similarity of the salts to which they give rise. They are all too reactive chemically to be found free in nature, and so must be prepared from their compounds. Under ordinary conditions, fluorine is a pale yellow gas, chlorine a greenish-yellow gas, bromine a dark reddish-brown liquid and iodine a gray crystalline solid—a deepening in color from fluorine to iodine, in the same order in which the atomic weights increase. Fluorine

is not easily liquefied, chlorine is easily liquefied, bromine is a liquid and iodine is a solid which turns directly to a purple gas on heating. Although fluorine behaves in an anomalous manner when dissolved in water, chlorine is fairly soluble in water, bromine but slightly so and iodine almost insoluble.

117 Preparing the Halogens

Fluorine has so little application in ordinary chemical reactions, is so difficult to prepare and so hard to keep that it does not represent the halogens so well as chlorine. Chlorine may be prepared by a variety of methods, such as heating its commonest acid (hydrochloric) with manganese dioxide:

$$4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2 \uparrow \qquad (35)$$

or by heating together common salt, concentrated sulfuric acid and manganese dioxide:

$$2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2 \uparrow \qquad (36)$$

Both these methods, which are easily carried on in the laboratory, are similarly applicable to bromine and iodine but not to fluorine.

The commercial preparation of chlorine (described more fully on page 415) involves the electrolysis of an aqueous solution of common salt. By this means both chlorine and hydrogen are evolved as gases, and a solution of sodium hydroxide (NaOH) is left behind:

$$2NaCl + 2H_2O + E \rightarrow H_2 \uparrow + Cl_2 \uparrow + 2NaOH \qquad (37)$$

where E is used to represent electricity.

Bromine and iodine may be obtained from their compounds by the use of chlorine gas. If a stream of chlorine gas is passed into aqueous solutions of potassium bromide and potassium iodide, the former will give up its bromine and the latter its iodine, coloring the solutions light brown and dark brown, respectively, while chlorine takes the place of these halogens. The following equations illustrate this:

$$Cl_2 + 2KBr \rightarrow Br_2 + 2KCl \qquad (38)$$

$$Cl_2 + 2KI \rightarrow I_2 + 2KCl \qquad (39)$$

After continued treatment, bromine and iodine will settle out at the bottom of the containers, the bromine as a deep reddish-brown

liquid, and iodine as gray plates. This is a cheap and convenient method of preparing these two halogens, which, in the pure state, are used on a large scale.

118 Chlorine

Of the four halogens, chlorine is the most commonly used. Fluorine and its compounds have by comparison little application, fluorine chiefly on account of its extraordinary activity, combining as it does with every known element and many compounds.

Chlorine forms many important compounds.

(1) An equal mixture of hydrogen and chlorine will explode in sunlight or diffused daylight to produce the colorless gas hydrogen chloride (HCl). This gas is very soluble in water, and its aqueous solution is known as hydrochloric acid, with the same formula HCl.

(2) Chlorine attacks all metals producing their chlorides; with copper, for example, it forms green cupric chloride ($CuCl_2$).

(3) With water chlorine at first forms a greenish solution, which slowly becomes colorless and bubbles of oxygen are given off. This reaction may be expressed by the equations:

$$H_2O + Cl_2 \rightarrow HCl + HOCl \tag{40}$$

$$2HOCl \rightarrow 2HCl + O_2 \tag{41}$$

In the first step two acids are produced, hydrochloric and hypochlorous. The hypochlorous acid is very unstable, liberating oxygen. If there is in contact with this hypochlorous acid any substance that may readily take oxygen into combination, the oxygen is liberated from the acid and taken up by that substance. This is the basis of the bleaching action of chlorine in the presence of water. Representing the chemical coloring matter by X, we have the following type of reaction:

$$X + HOCl \rightarrow XO + HCl \tag{42}$$

The chances are that the oxidized coloring matter (XO) is colorless or nearly so; hence the bleaching action of moist chlorine. A similar reaction occurs on passing chlorine into an alkaline solution. Thus

$$Cl_2 + 2NaOH \rightarrow H_2O + NaCl + NaOCl \tag{43}$$

Besides water and sodium chloride, we obtain sodium hypochlorite, the sodium salt of hypochlorous acid. This salt is much more

stable than the acid, though it also releases nascent oxygen which acts as above not merely to bleach colored bodies but also to kill bacteria and destroy (oxidize) noxious refuse generally.

A curious compound may be obtained by treating lime (calcium oxide, CaO) with dry chlorine. A yellowish powder results, known technically as chloride of lime, an anomalous type of compound. It may be regarded as the calcium salt of two acids, hydrochloric and hypochlorous, and its formula may best be represented in a graphical manner as follows:

$$\mathrm{CaO} + \begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl} \end{array} \rightarrow \mathrm{Ca}\begin{array}{l} \diagup \mathrm{Cl} \\ \diagdown \mathrm{OCl} \end{array} \tag{44}$$

This compound may be made to give off either its oxygen or its chlorine by appropriate treatment. Actually its odor indicates its instability, for it smells strongly of chlorine. Hence it is used for bleaching and for the sterilization of refuse undergoing bacterial decomposition.

There are some interesting experiments that can be performed with jars of chlorine gas.

(1) Into a jar of the gas plunge a burning taper. It will continue to burn, but with a smoky flame. The wax of the taper contains compounds of carbon and hydrogen which split apart, the hydrogen to combine with the chlorine and the carbon to be set free as black particles. This is an example of combustion where oxygen is not one of the reacting substances and where the combustion is not complete.

(2) Moisten a piece of blue litmus paper and put it in a jar of chlorine. The blue quickly turns to red and then to a straw-yellow. The red indicates that chlorine has combined with the water on the litmus paper to form an acid, and that bleaching of this red coloring matter occurs subsequently.

(3) A piece of yellow phosphorus [1] burns vigorously in chlorine to give a white compound, PCl_5, phosphorus pentachloride.

(4) Fine particles of metallic antimony, when shaken into chlorine, glow in a scintillating manner and combine to form a yellow-

[1] Yellow phosphorus should not be handled or used by an inexperienced student, or at all unless carefully supervised.

white powder, antimony trichloride ($SbCl_3$), with evolution of heat.

119 Hydrochloric Acid (HCl)

This acid, formerly called muriatic acid, is widely used industrially. It is commonly prepared by allowing concentrated sulfuric acid to act on common salt:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow \tag{45}$$

The hydrogen chloride so produced is dissolved in water up to 35 per cent by weight and the solution sold as hydrochloric acid.

The fact that the formula HCl is used here in connection with two names may well occasion some confusion. An acid, as we shall see later, displays the characteristics of acids only in the presence of water or some liquid closely related to water and hence are called acids in that connection. When the gas HCl is dissolved in water it behaves as an acid; but when it is a pure dry gas it does not act as an acid at all and so we give it the name derived from the two elements which produced it, hydrogen and chlorine.

120 Nomenclature

The halogens tend to form acids which also contain oxygen. They are of different degrees of importance, but those of chlorine are given here because of their importance in chemical nomenclature. The name of the sodium compound or salt is given with its formula:

HCl, hydrochloric acid, a compound of hydrogen and chlorine only; NaCl, sodium chloride.
HOCl (unstable), hypochlorous acid; NaOCl, sodium hypochlorite.
$HClO_2$ (unstable), chlorous acid; $NaClO_2$, sodium chlorite.
$HClO_3$ (unstable), chloric acid; $NaClO_3$, sodium chlorate.
$HClO_4$ (stable), perchloric acid; $NaClO_4$, sodium perchlorate.

Of these four *oxyacids*, chloric acid contains the normal quantity of oxygen that is to be expected according to considerations of valence—hence the name chloric ends in *ic*. Chlorous acid contains the next quantity of oxygen less than that associated with the termination *-ic*. Hypochlorous acid contains less oxygen even

than chlorous acid; hence the prefix *hypo-* and the suffix *-ous*. Perchloric acid contains an abnormally large proportion of oxygen; hence the prefix *per-* and the suffix *-ic*.

121 What Is a Salt?

The word salt is used above in its general sense, that is, it is the normal result when an alkali and an acid react together. This reaction may be illustrated in this way. A definite quantity of sodium hydroxide, having, like alkalies, the property of turning red litmus blue, when treated with a proper quantity of hydrochloric acid, which turns blue litmus red, loses this alkaline property and also causes the acidic property of the acid to disappear. Water and a compound, sodium chloride, are obtained, as shown by the equation:

$$NaOH + HCl \rightarrow H_2O + NaCl \tag{46}$$

This sodium chloride, undoubtedly the first salt known to man and now known as *common salt*, has the properties neither of the alkali nor of the acid from which it has been formed by the process of interchange of OH for Cl, that is, the process of *double decomposition with formation of water*. Inasmuch as the alkali has destroyed the acidic properties of the acid and the acid the alkaline properties of the sodium hydroxide, this reaction is known as *neutralization*.

122 Bromine and Iodine

Bromine at room temperature has a high vapor pressure, as indicated by the brown vapor always floating over the surface of liquid bromine. Iodine, though a solid, has above it likewise a vapor which is purple; and, if iodine is heated, all the gray solid will be seen to pass completely into purple vapor. This vapor on cooling changes back again into fine, grayish crystals. Both these changes, from solid to gas and back again, occur at ordinary pressures without the intermediate formation of liquid iodine. This uncommon occurrence, known as *sublimation*, provides an excellent method for the purification of iodine. Should these crystals be heated under sufficient pressure, however, the iodine will first melt like most other solids before changing to vapor.

Bromine and iodine are much more soluble in chloroform ($CHCl_3$) than in water. The bromine gives its own color to the solution; the iodine-chloroform solution is purple. Iodine can be identified easily by its peculiar action on starch solution, where it

produces a blue to black coloration if the mixture is cold and non-alkaline, that is, either neutral or acid. Iodine, when dissolved in potassium iodide solution and alcohol, is widely used as an antiseptic, since its 5 per cent solution possesses the most powerful disinfecting action of all such reagents.

Bromine and iodine react somewhat similarly to chlorine when dissolved in sodium hydroxide solution, but their action is not nearly so vigorous.

123 Common Halides

Each of the halogens combines with a large number of elements to form compounds. Among these elements is hydrogen, which combines most vigorously with fluorine and least so with iodine. The compounds so formed, the halogen hydrides, are known as hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr) and hydrogen iodide (HI). These are colorless gases, extremely soluble in water, and their aqueous solutions behave as strong acids. These acids are named hydrofluoric, hydrochloric, hydrobromic and hydriodic, respectively. Their compounds with metals, for example, sodium, are named as follows: NaF, sodium fluoride; NaCl, sodium chloride; NaBr, sodium bromide; and NaI, sodium iodide. Similar compounds are known of potassium, calcium, aluminum, etc.

Hydrofluoric acid has the uncommon property of attacking glass, since it forms with the silica (SiO_2) of glass the volatile silicon tetrafluoride (SiF_4), thereby causing the decomposition or etching of glass. Hence it is always kept in a bottle made of hard paraffin or rubber which is not so attacked.

Hydrobromic and hydriodic acids gradually turn brown on exposure to light and air. Otherwise all four acids are colorless. Chlorides, bromides and iodides are detected by addition to an aqueous solution of silver nitrate ($AgNO_3$). In each case a precipitate is formed, consisting of silver chloride, or bromide or iodide, none of which is more than very slightly soluble in water. The equations representing these reactions are:

$$AgNO_3 + HCl \rightarrow HNO_3 + AgCl \downarrow \text{ (white)} \tag{47}$$

$$AgNO_3 + HBr \rightarrow HNO_3 + AgBr \downarrow \text{ (pale yellow)} \tag{48}$$

$$AgNO_3 + HI \rightarrow HNO_3 + AgI \downarrow \text{ (yellow)} \tag{49}$$

At the same time the compound HNO_3, nitric acid, is produced, but remains dissolved and invisible.

124 The Halogens in Photography

The silver salts of chlorine, bromine and iodine rapidly change color on exposure to light, becoming gradually darker. This property is employed in photography. In the first instance a plate or film suitably coated with a silver halide, for example, the bromide ($AgBr$), is exposed in a camera to the light emanating from some object of which an image is desired. White objects reflect more light than dark ones, with the result that they send more light through the camera lens to the silver bromide coating than the dark objects. This plate or film carrying the invisible or latent image is then subjected to a so-called reducing agent which develops the image on the film so that more metallic silver appears where light from bright objects struck than from the darker portions. Unused silver bromide is then dissolved out by means of photographer's hypo (sodium thiosulfate, $Na_2S_2O_3$), and this fixing produces the negative, as it is called. The negative has the lights and darks reversed from what they were in the objects photographed. They are again reversed by exposing to the light another film of silver halide (this time on paper, perhaps) behind the negative, with the result that the dark portions of the negative shade the film and the lighter portions allow most light to pass through. The resulting positive, which has the shading of the photographed object now correct, after being developed (if necessary), fixed, tinted, etc., is the finished product.

125 The Halogens and Health

Sodium chloride, a necessary constituent of body fluids, is continuously given off by the kidneys and the sweat glands; consequently, it must be replaced by our food. Meat juices aid in supplying it. Grazing cows, it appears, get an insufficient amount of sodium chloride. To remedy this deficiency, they are often given blocks of salt, known as "salt licks." Salt is also frequently added to hot weather drinks to make up for the sodium chloride lost through the sweat glands.

Chlorine gas is used to a great extent in the purification of water in cities. The water from a river, for example, is directed into large, underground settling tanks; here suspended mud tends to

settle out, taking with it quantities of bacteria which may have a deleterious effect upon the health. In order to insure complete safety for the consumer, this water is treated by passing chlorine into it from tanks of the compressed gas just before it enters the water mains. The action of chlorine in forming the unstable hypochlorous acid provides the agent which destroys bacteria in much the same manner as a dye is bleached, as explained above. The small amount of hydrochloric acid remaining in the water is insufficient to harm the consumer especially since (1) many natural waters contain dissolved calcium compounds which neutralize this acid and (2) the human stomach requires small amounts of hydrochloric for the digestion of food.

Besides chlorine, sodium hypochlorite as in "Javel Water" is used not merely to whiten clothes during washing but also to destroy bacteria in them. Specially stabilized hypochlorite solutions of the appropriate strengths are used for disinfecting the mouth and also wounds.

Chloride of lime is not very soluble in water and when left exposed to the atmosphere gives off large quantities of chlorine. It is much too harsh to be used on human tissues but is a necessity for garbage and similar refuse.

Bromine is very unsafe to handle because of its corrosive action on animal tissues. Potassium bromide (KBr) is used medicinally as a mild sedative.

Iodine, as previously stated, is used to destroy bacteria. In large concentration its continued action on the tissues can be very painful and corrosive; for which reason it is made up in suitable percentages in solution and these solutions are sold under supervision.

Silver iodide (AgI) is used as a powerful internal disinfectant in certain special cases.

Sodium fluoride (NaF) is definitely toxic and, though never used on human beings, is commonly used to kill cockroaches.

Potassium iodide (KI) is now a common constituent of common salt for household use. It tends to supply the quantity of iodine required to keep the thyroid gland healthy.

In the foregoing recital we have made it clear that the halogens play an important part in human health by the destruction of bacteria. Bacteria are minute forms of animal life whose reproduction can be deleterious to our health, although it does not follow

that all bacteria are harmful. There are two methods of controlling bacteria: (1) by destroying them outright, in which case we call the reagent which does this a *disinfectant*; (2) by preventing their spread and reproduction. Reagents which perform this second function are called *antiseptics*. The two characteristics of a good disinfectant or antiseptic are (1) that it be effective and (2) that it be not harmful to the tissues. These characteristics determine which of the above (and of the many others known) should be used in any particular case.

126 Review of Definitions

An acid is a compound between hydrogen and a non-metal with or without oxygen. The hydrogen may be replaced by a metal (or its equivalent).

A salt is the resulting compound when the hydrogen of an acid is replaced by a metal or its equivalent.

A halogen is any one of the four elements fluorine, chlorine, bromine and iodine.

A halide is any compound of a halogen.

An antiseptic is a substance, or mixture of substances, which will render bacteria inactive.

A disinfectant is a substance, or mixture of substances, which will destroy bacteria. A germicide is what the word implies—germ-killer—and is often used alternatively here.

A chemical group is a number of elements found in one of the vertical columns of the Periodic Table. The elements in such a group show more similarities than dissimilarities in their chemical and physical properties, these properties showing a gradation from first to last.

127 Summary

The elements are classifiable into groups or families, of which the halogens are an important unit. These halogens are fluorine, chlorine, bromine and iodine.

The halogens show a gradual transition in physical properties from fluorine to iodine. In chemical behavior the same generalization holds; fluorine is the most active and iodine the least. The halogens may replace each other from their compounds in the order F, Cl, Br, I.

Chlorine is the commonest of the four halogens. It may be prepared from its salts by electrolysis. It combines with hydrogen, phosphorus, antimony and many other elements with great vigor, forming chlorides.

Chlorine unites with water to form two acids—hydrochloric (HCl) and hypochlorous ($HOCl$). The latter is unstable and may lose its oxygen to bleach organic coloring matter by oxidation.

The halogens form hydrides (HF, HCl, HBr, HI) which dissolve in water to form acids.

The silver salts of chlorine, bromine and iodine are sensitive to light and are therefore the basis of photography.

The halogens, the basis of many useful medicinal materials, are closely associated with our individual and national health.

Questions

1. Explain the significance of the terms hydrogen chloride and hydrochloric acid.
2. Compare, in tabular form, the properties of the halogens.
3. What significance have the prefixes *per-* and *hypo-*, and the suffixes *-ic* and *-ous*?
4. Explain the bleaching action of chlorine.
5. By what methods may chlorine be prepared?
6. How may chlorine be used to prepare bromine and iodine?
7. How are the halogens and their compounds used in public health?
8. If chlorine is used to purify water in a city's water intake system, would it still contain chlorine when you draw it out of the faucet in your home? Why?

10

Molecular and Atomic Weights

128 Molecular Weights

In Chapter 6 we quoted Avogadro's gas law—that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. A most useful deduction from this law allows us to formulate a system which relates the volume of a gas to its molecular weight. We have seen (Chapter 3) that the

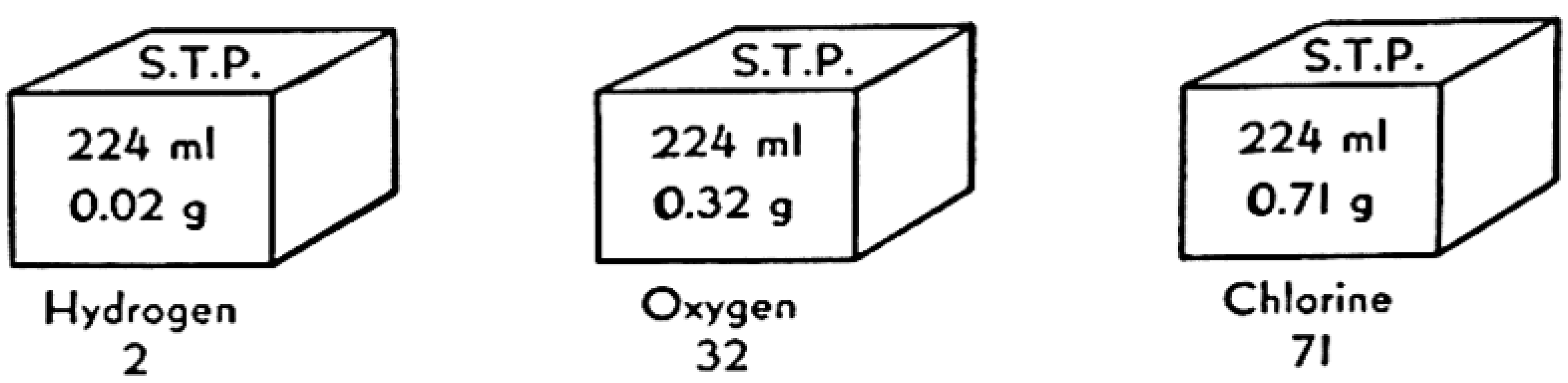


FIG. 36. Equal volumes of these three gases at the same temperature and pressure contain the same number of molecules; hence these weights represent the relative weights of the individual molecules.

density of a gas may be found by weighing a known volume of it at a fixed temperature and pressure and relating it to some standard. In Fig. 36 are illustrated the weights of equal volumes of three gases, hydrogen the lightest of all known gases, oxygen and chlorine. Since these equal volumes at the same temperature and pressure must, according to Avogadro's law, contain the same number of molecules, these weights represent not merely the weight of each volume of gas, but the ratio of the weights of one molecule of hydrogen, one molecule of oxygen and one molecule of chlorine. Because of the volumes involved in well-known gas reactions, each molecule of these gases was found to contain 2 atoms per molecule. In order to have a unitary system of molecular weights, the volume

occupied by 2 grams of hydrogen (actually 2.016 grams) at 0°C and 760 mm mercury pressure was calculated: this value was found to be 22,400 ml (22.4 liters). Such a volume of oxygen would weigh 32 grams and the same volume of chlorine 71 grams. These values are called *gram molecular weights*, and the 22.4 liter volume is known as the *gram molecular volume* because it is actually the volume that the molecular weight of a gas expressed in grams occupies at standard temperature and pressure.

The gram molecular weights without the word "gram," that is, molecular weights, are numbers which represent the relative weights of molecules based on the lightest gas hydrogen taken as 2. Air is not a single compound but a mixture of gases. Its density can be found as above, and a practical molecular weight can be assigned to it, namely, 28.8. Thus by Dumas' method (§ 29) we can find the molecular weight of any gas.

129 Proof of the Diatomic Nature of an Elementary Gas

As a matter of interest the following proof is given that the molecule of an elementary gas may contain two atoms (see § 112).

It is shown by an actual experiment that one volume of hydrogen added to one volume of chlorine will give two volumes of hydrogen chloride. All three substances are gases, and these volumes are at the same temperature and pressure. Using the simplest equation, we have

$$H + Cl \rightarrow 2HCl$$

By analysis we find that a hydrogen chloride molecule contains one atom of hydrogen and one atom of chlorine. Let us insert practical volumes in this equation:

$$\underset{100\text{ ml}}{H} + \underset{100\text{ ml}}{Cl} \rightarrow \underset{200\text{ ml}}{2HCl}$$

The number of molecules in 100 ml of hydrogen will be the same as in 100 ml of chlorine (by Avogadro's law). By the same law, the 200 ml volume of HCl will contain *twice* the number of molecules. Suppose we give sample values to these molecules:

$$\underset{\substack{100\text{ ml}\\100\text{ molecules}}}{H} + \underset{\substack{100\text{ ml}\\100\text{ molecules}}}{Cl} \rightarrow \underset{\substack{200\text{ ml}\\200\text{ molecules}}}{2HCl}$$

But we have said that each molecule of HCl contains one atom of hydrogen and one of chlorine. Hence we can go one step further:

$$\underset{\substack{100\text{ ml}\\100\text{ molecules}}}{H} + \underset{\substack{100\text{ ml}\\100\text{ molecules}}}{Cl} \rightarrow \underset{\substack{200\text{ ml}\\200\text{ molecules}}}{2HCl}$$

These 200 atoms of hydrogen must have been originally in the 100 molecules; similarly, the 200 atoms of chlorine must have been originally in the 100 molecules. The only explanation is that the 100 molecules of hydrogen must have contained 200 atoms of hydrogen, or 2 atoms in each one molecule. Similarly, the molecule of chlorine must contain 2 atoms. We can now write the equation correctly:

$$H_2 + Cl_2 \rightarrow 2HCl \tag{50}$$

130 Atomic Weights

We have seen how, by finding the weight of 22.4 liters of an elementary gas at standard temperature and pressure, we obtain a value which can be suitably called the gram molecular weight. In addition, we can find the gram atomic weight of that gas, if there are two atoms to the molecule, merely by dividing the molecular weight by 2. This gives us a beginning for our system of atomic weights even if we have never actually seen or weighed an atom. We make the distinction between molecules and atoms in the following statements. *A molecule is the smallest particle of a pure chemical substance which can exist free and alone, whereas an atom is the smallest particle of an element which can be found entering into chemical combination with another atom.* The numerical value which we call atomic weight is *not* the weight of an atom in any of our practical systems of weights such as the grain or the gram or the ounce, because an atom weighs far too little to be measured in such terms. The atomic weight of oxygen is given as 16 because it has that value compared with hydrogen, if we call the latter 1.

The methods for finding atomic weights are: (1) from Avogadro's law and by analysis; (2) from Dulong and Petit's law; (3) from the equivalent weight and the valence.

These methods are detailed below, using the element carbon as an example of the element whose atomic weight is to be found.

(1) We first find the gram molecular weights of a number of

gases in which carbon is one of the constituents; we analyze these gaseous compounds and put down the weight of carbon found in the gram molecular weight. From these values we find the smallest weight of carbon present in any of the compounds. Such values are shown in the table which follows:

TABLE 6

Compound	*Gram Molecular Weight*	*Carbon Alone*
Carbon monoxide	28	12
Carbon dioxide	44	12
Benzene	78	72
Alcohol	46	24
Chloroform	118.5	12

The smallest weight of carbon in the third column is 12; it is taken as the atomic weight of carbon.

(2) Dulong and Petit's law states that *in general the atomic weight of an element multiplied by its specific heat is equal to a constant*, or

$$\text{Atomic weight} \times \text{Specific heat} = K$$

This K, called the atomic heat, has a value of nearly 6.4. Therefore,

$$\text{Atomic weight} = \frac{6.4}{\text{Specific heat}}$$

The specific heat is easily found, particularly in the case of a solid; hence the atomic weight can be calculated.

(3) The determination of the equivalent weight is made in a variety of ways, but it is necessary to define the term first. An example will provide us with the definition. If the gram molecular weight (G.M.W.) of water is analyzed, it will be found that 2.016 grams of hydrogen are united with 16 grams of oxygen in 18.016 grams of water. Hence the formula H_2O.

Hydrogen (1.008) is taken as the unit of atomic weight. Since 2.016 grams are found here combined with 16 grams of oxygen, it follows that 1.008 grams would combine with $\frac{16}{2}$ or 8 grams of oxygen. Hence 8 is the equivalent weight of oxygen. Another name for equivalent weight is combining weight since hydrogen

and oxygen do combine together. The term equivalent weight, however, can be used for elements (and even compounds) which do not combine with hydrogen. Eight grams are the equivalent in combining power of 1 gram of hydrogen; consequently any element which does not combine with hydrogen may be found to combine with oxygen. The weight of that element which combines with 8 grams of oxygen is its equivalent weight. We have seen that the atomic weight of oxygen is 16 and its equivalent weight is 8. If we divide the former by the latter we get the value 2:

$$\frac{\text{Atomic weight}}{\text{Equivalent weight}} = \frac{16}{8} = 2$$

We see this 2 in the formula H_2O; that is, *2 is the number of hydrogen atoms with which 1 atom of oxygen will unite* in forming the stable compound water. This number *2* is called the *valence* of *oxygen.* Therefore,

$$\text{Valence} = \frac{\text{Atomic weight of element}}{\text{Equivalent weight of element}}$$

or, in other words, valence is a number denoting the number of hydrogen atoms which will be found united with one atom of another element. The above equation may also be written:

$$\text{Equivalent weight} \times \text{Valence} = \text{Atomic weight}$$

Thus hydrogen, the unit of density and the unit of atomic and molecular weights, becomes the unit for equivalent weights and also the unit of valence. *Equivalent weight* can in general be defined as *the weight of an element which combines with* (or replaces or otherwise reacts with) *1.008 grams of hydrogen or 8 grams of oxygen. Valence* then becomes *the capacity of one atom of an element to combine with atoms of hydrogen.*

We may now find the atomic weight of an element by finding its equivalent weight and its valence.

131 Valence

We have spent considerable time explaining how atomic weights are found although we may never find one or need to find one; for that is well looked after by an international committee. But the chief advantage to us is that we were thereby introduced to the doctrine of valence. This we have already defined exactly in

terms of hydrogen, affording us (1) a means of reading valence by inspection of formulae and (2) a system of writing formulae of compounds we do *not* know when we *do* know the valence of the elements involved.

In the formulae H_2S, NH_3, PH_3, HCl the valence of S is 2, of N 3, of P 3 and of Cl 1. In the formulae NO, N_2O_3, SO_2, SO_3, Al_2O_3 the valence of nitrogen is 2 and 3, of sulfur 4 and 6 and of aluminum 3. In these instances each oxygen atom has a valence of 2, and the valence of other elements is calculated therefrom.

The term valence may also apply to radicals. In HNO_3, the NO_3 radical has a valence of 1; in H_2SO_4, the SO_4 radical has a valence of 2.

If Al has a valence of 3 and S has a valence of 2, take the least common multiple of 2 and 3 (which is 6) and divide this by the valence of each element in the formula. The dividend is the number of atoms of each element in the compound:

$$\mathrm{Al} = 6 \div 3 = 2 \qquad \mathrm{S} = 6 \div 2 = 3$$

Hence Al_2S_3. Again, if Ca has a valence of 2 and the radical PO_4 a valence of 3 (as in H_3PO_4) we proceed as before. The least common multiple here is 6.

$$\mathrm{Ca} = \tfrac{6}{2} = 3 \qquad (\mathrm{PO_4}) = \tfrac{6}{3} = 2$$

Therefore the formula is $Ca_3(PO_4)_2$. This is a rule which can frequently be applied.

132 Methods of Determining Molecular Weight

In the previous pages we observed that no accurate value for the atomic weight of an element can be found until the molecular weights of compounds of that element have been determined. Relatively few compounds are gases at ordinary conditions, so that it is necessary to have molecular weight methods for liquid and for solid compounds. If a liquid can be turned into a gas at not too great a temperature or too low a pressure to allow accurate measurements to be made, it is not difficult to read the weight, volume, temperature and pressure of the gas and, by calculation, to find the gram molecular volume at standard temperature and pressure. This is the volume occupied by the liquid *if it existed as a gas at standard temperature and pressure*, and the weight of this volume is taken as the molecular weight.

If the compound is not volatile, that is, is not easily turned into gas, it may be possible to dissolve it in a liquid (perhaps water) and find out its effect on the freezing point or on the boiling point of that liquid. These methods are shown in Chapter 13.

133 Formula Weight

In some instances we may have to deal with substances which (1) cannot be volatilized without decomposing and (2) which cannot be dissolved in any known solvent without decomposition. Such a substance is calcium carbonate. We have therefore no way of finding the true molecular weight. But this is no great disadvantage because the only occasions on which we must know the exact molecular weight of a substance is when we want to use it either in the gaseous state or dissolved in some solvent. What we do, then, if the substance is calcium carbonate, is to analyze it, find its exact composition and write down the simplest possible formula—in this case $CaCO_3$—rather than $Ca_2C_2O_6$ or $Ca_3C_3O_9$, etc.

134 To Find the Correct Formula of a Compound

An example will allow us to formulate the correct procedure when dealing with an unknown compound.

Example. A compound when analyzed showed the following percentages by weight: carbon, 40 per cent; hydrogen, 6.67 per cent; oxygen, 53.33 per cent. Its molecular weight was found to be 60. What is its correct formula?

Divide the percentages above by the appropriate atomic weight and simplify the atomic ratios so found, as in the following tabulation.

Element	*Percentage*	÷	*Atomic Weight*	=	*Atomic Ratio*	
Carbon	40	÷	12	=	3.33)	(1
Hydrogen	6.67	÷	1	=	6.67)	(2
Oxygen	53.33	÷	16	=	3.33)	(1

The *simplest* formula is CH_2O; the *correct* formula may also be $C_2H_4O_2$ or $C_3H_6O_3$, etc. The molecular weights of these would be 30, 60 and 90, respectively. But the molecular weight given was 60. Therefore the correct molecular formula is $C_2H_4O_2$. If, however, no way had been known of finding the molecular weight, the only formula would have been the simplest—CH_2O. Fortu-

nately the molecular weights of both the substances represented by CH_2O and $C_2H_4O_2$ can be found by gaseous methods. But it would be unfortunate if this were not so, since CH_2O stands for formaldehyde and $C_2H_4O_2$ for acetic acid, both very different compounds physically and chemically.

Sometimes the analysis is given according to the weight of each element represented; then we change these values to percentages before proceeding as in the tabulation above.

We may now trace the steps to be followed in obtaining the correct formula of a compound:

(1) Find its molecular weight if at all possible.
(2) Analyze it so as to obtain the weight of each element present in a known weight of it.
(3) Change these individual weights to percentages.
(4) Divide each percentage by the atomic weight of the appropriate element; this gives a set of figures representing the atomic ratios.
(5) Simplify this ratio and include the values in a formula; this is the simplest formula.
(6) Calculate the molecular weight of this formula by adding the atomic weights. Write multiple formulae and their molecular weights.
(7) Compare the determined molecular weight with the figures in (6). The identity of the correct formula is apparent.

135 Advantages of the System Based on Hydrogen

The advantages of having a system of atomic and molecular weights based upon a single unit are many. Hydrogen, the lightest of all known substances, is, as we have seen, the unit for atomic weight (1.008), for equivalent weight (1.008), for molecular weight (2.016) and for valence (1). It is true that for certain practical purposes, such as involve weighing in the presence of air, oxygen is the practical unit. Oxygen, however, is divalent, and we finally relate our practical values to hydrogen because of the greater convenience involved.

Avogadro's law shows that the gram molecular volume (G.M.V.) of different gases at standard temperature and pressure (S.T.P.) contains the same number of molecules. Since this G.M.V. was arbitrarily chosen as the volume to contain at S.T.P. the gram

molecular weight (G.M.W.), it follows by inference that the G.M.W. of all substances will contain the same number of molecules whether these substances are gases, liquids or solids. Of course the G.M.V. will not hold for liquids and solids for it is founded on the gas laws, which do not hold for liquids or solids. But it is reasonable to suppose that the G.M.W. of a liquid or solid will contain the same number of molecules as the G.M.W. of a gas.

The following example should justify this.

Example. The G.M.W. of lime (56 grams of CaO) are dissolved in water in a large container which can be made air-tight. To this solution is added the G.M.W. of carbon dioxide (44 grams of CO_2, the G.M.V. at S.T.P.) and the vessel is sealed. After it is shaken thoroughly, a heavy white precipitate is formed. Examination of the gaseous contents of the vessel will show that *all* the carbon dioxide has disappeared. Also, filtering, drying and weighing the white precipitate will disclose that it is calcium carbonate ($CaCO_3$) and weighs 100 grams. In equation form this is expressed as follows:

$$\underset{\substack{\text{44 grams}\\ \text{G.M.W.}\\ \text{G.M.V. at S.T.P.}}}{CO_2} + \underset{\substack{\text{56 grams}\\ \text{G.M.W.}}}{CaO} \rightarrow \underset{\substack{\text{100 grams}\\ \text{formula weight}}}{CaCO_3\downarrow} \qquad (51)$$

Since the G.M.V. of CO_2 must contain Avogadro's number of molecules, it follows that the G.M.W. of lime must have contained the same number of molecules although lime is a solid.

Many such examples justify our belief that the G.M.W. of any substance must contain the same number of molecules. If any of them did not, something would be left over in a chemical reaction. A chemical reaction can therefore be represented by an equation that shows a *real* equality of masses on each side of the equal sign. This equation is quite consistent with the laws of conservation of mass and of constant composition (also known as the law of definite proportions).

136 Summary

The molecular weight of a gas may be found (1) by weighing a known volume of it at known temperature and pressure, (2) by calculating the correct volume at S.T.P. and (3) by calculating from this corrected volume and the observed weight the weight of 22.4 liters at standard temperature and pressure.

The molecule of elementary gases (except He, A, Ne, Kr, Xe) contains 2 atoms.

A molecule of any substance is the smallest particle of it which can exist free and alone. Atoms, on the other hand, are the smallest particles of an element which can enter into and come out of chemical combination. Usually they are not found existing free and alone for they are as a rule too active to remain unattached. If there is no other atom which they may join, they pair up among themselves.

Dulong and Petit's law holds chiefly for metals. It states that the atomic weight multiplied by the specific heat is equal to a constant (about 6.4). This helps us to calculate the atomic weight of a metal when it is difficult to find suitable compounds for analysis and where the metal has more than one valence.

The atomic weight system is based on hydrogen (1.008). When an element is monovalent the atomic weight is the same as the equivalent weight since the basis is the same. But when the element has a valence greater than one or has more than one valence, the equivalent weight will be a fraction of the atomic weight; the reciprocal of this fraction is the valence.

The formula weight is the simplest molecular weight available from the analysis. It is satisfactory for all quantitative purposes but it does not tell us the size of the molecule.

Questions

1. Define molecular weight, atomic weight. How are they related in elementary gases?
2. How may the molecular weight of a gaseous substance be found when the density is known?
3. How does Dulong and Petit's law aid in finding atomic weights?
4. What relationships exist between atomic and equivalent weight? What is valence?
5. How is gram molecular weight related to the gram molecular volume?
6. Using the following atomic weights, calculate the equivalent weight of the elements designated: N, 14; S, 32; O, 16; P, 31; Ca, 40. (*a*) Nitrogen in (*a*) N_2O and (*b*) NH_3. (*b*) Sulfur in (*a*) H_2S and (*b*) SO_2. (*c*) Phosphorus in (*a*) PH_3 and (*b*) P_2O_5.
7. (*a*) 67.2 ml of arsine, measured at S.T.P., weighs 0.234 gram. Calculate the molecular weight. (*b*) 623.6 ml of phosgene, measured at 117°C and 780 mm, weighs 1.98 grams. Calculate its molecular weight.
8. (*a*) The specific heat of mercury is 0.0336. Calculate its approximate atomic weight. (*b*) The atomic weight of nickel is 58.69. Calculate its specific heat.
9. If the valence of oxygen is 2, of barium is 2, of (PO_4) is 3, of (SO_4) is 2, of Mg is 2, of Al is 3, correct the following formulae: $Ba(PO_4)$; Mg_2O_3; $Al_3(SO_4)_2$; $Mg_2(SO_4)_3$; Ba_3O_4.

11

Sulfur and Its Compounds

137 Where It Is Found

This element sulfur occurs widely in the earth's crust free and combined with a large number of metals. In the free state it is found in substantial quantities in the vicinity of both active and extinct volcanoes. In combination it is found chiefly as the sulfide and the sulfate when linked to such elements as iron, mercury, copper, zinc, calcium and barium. In the products of living cells it also occurs combined to the extent of about 1 per cent, for example, in eggs and some vegetable oils.

138 How It Is Obtained

One source of sulfur is the volcanic deposits. Where the sulfur lies near the surface mixed with rock, masses of this aggregate are piled up in kilns and set alight. The slow combustion of part of the sulfur produces enough heat to melt the residue, which flows away from the kiln and is suitably collected. In another type of underground deposit not related to volcanoes, the sulfur is melted by superheated steam and blown to the surface by the Frasch process (§ 441). Purification, if necessary, is carried on by heating, when the sulfur at first melts and then volatilizes. The vapors are later condensed in a cool chamber. The first product of this distillation is a mass of fine crystals called flowers of sulfur; later the element appears on the floor of the collection chamber as a liquid. Thence it is run into molds, where it cools, forming solid cylinders known as roll sulfur; or it may be allowed to cool and solidify outdoors in large enclosures.

139 Allotropy of Sulfur

If some flowers or roll sulfur are dissolved in carbon disulfide and allowed to crystallize by evaporation of the solvent, *rhombic*

crystals separate out. If these crystals are heated to 114.5°C they melt. After further heating and then slowly cooling this mass until about half of it becomes solid, and after pouring off the molten part, we see that the residue consists of long, needle-shaped crystals. It is known as the *monoclinic* form of sulfur.

Again, if hot molten sulfur is poured into cold water, it partially solidifies to give a brown, elastic, rubber-like substance—*plastic* sulfur—without crystalline form, that is, amorphous.

Thus sulfur can exist as a solid in three allotropic modifications. An analogous phenomenon was observed with carbon, but with sulfur it is found that these modifications are easily interconvertible. For if rhombic sulfur is kept between 95° and 114.5°C, it will gradually change spontaneously to the monoclinic form. Again, if these monoclinic crystals are kept at some temperature below 95°C, they will slowly assume the rhombic form. Also plastic sulfur gradually turns into yellow rhombic crystals if left at some temperature below 95°C, or to monoclinic if kept above this temperature.

140 Other Properties of Sulfur

The solid forms of sulfur melt at 114.5°C and boil at 444.5°C to form yellow vapors. Solid sulfur is brittle, with a specific gravity of about 2, and is soluble only in carbon disulfide (CS_2), from which it may be recrystallized as stated previously. Sulfur is slowly oxidized at ordinary temperatures in moist air, but burns vigorously to form the gas sulfur dioxide.

$$S + O_2 \rightarrow SO_2 \tag{52}$$

This is its chief use either in the treatment of wood pulp or in the manufacture of sulfuric acid.

141 Hydrogen Sulfide

Hydrogen and sulfur do not readily unite, but their compound (H_2S) may be easily prepared by acting on iron sulfide with dilute hydrochloric acid, ferrous chloride being formed at the same time:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \tag{53}$$

Hydrogen sulfide is a colorless gas, with a distinctive odor, commonly referred to as the odor of rotten eggs. It is highly poisonous, inhalation of 1 part in 200 for a considerable time proving fatal.

Fortunately, however, the odor is so intense and nauseating that the gas renders those exposed to it highly uncomfortable long before its concentration becomes dangerous. When dissolved in water it forms a weak acid, whose chief use is in the precipitation of insoluble sulfides of metals. These sulfides, being for the most part highly colored, serve as tests for the metals concerned. For example, arsenious sulfide (As_2S_3) is bright yellow, zinc sulfide (ZnS) is white, manganous sulfide (MnS) pale pink and antimony sulfide (Sb_2S_3) orange-red. Thus hydrogen sulfide is of considerable use in detecting the presence of metals in solutions of their salts, that is, in qualitative analysis.

Hydrogen sulfide is found dissolved in the water of certain springs, and has been thought for many years to possess medicinal properties. This aqueous solution is slowly oxidized in contact with the atmosphere to give rise to a deposit of sulfur. In the gaseous state hydrogen sulfide burns in air or oxygen to form water and sulfur dioxide.

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \tag{54}$$

142 Sulfur Dioxide

This compound may be prepared by burning sulfur in air or oxygen (§ 44), by the roasting of sulfides of iron, copper, etc., in a stream of air and by a number of less direct methods.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \tag{55}$$

represents the formation of sulfur dioxide when ores rich in sulfur are roasted to obtain the metals from them. In some localities where this smelting is carried on, the evolved gas is utilized for the manufacture of sulfuric acid.

Sulfurous Acid. Sulfur dioxide is a colorless, choking gas with a sour taste, and dissolves readily in water to form a weak acid, sulfurous acid:

$$H_2O + SO_2 \rightarrow H_2SO_3 \tag{56}$$

This compound is easily decomposed by heat, reversing the process indicated in the equation above. In the presence of moisture sulfur dioxide tends to take up oxygen to form sulfuric acid (H_2SO_4). It is thus a reducing agent, since it picks up oxygen, and this action is utilized in bleaching organic coloring matter and in the destruction of bacteria.

143 Sulfuric Acid

Sulfur dioxide combines but slowly with oxygen to form sulfur trioxide (SO_3) under ordinary circumstances; but at a high temperature and in the presence of a suitable catalyst this reaction takes place much more rapidly. The resulting solid sulfur trioxide (SO_3) combines with water to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (57)$$

These generalizations are utilized in the large-scale production of sulfuric acid by the modern Contact process.

Contact Process. This process consists of bringing a mixture of sulfur dioxide and oxygen (from the air) into contact with a platinum surface at 400°C. The resulting sulfur trioxide on solution in 98 per cent sulfuric acid gives oleum or fuming sulfuric acid, which on dilution with water provides the market with the sulfuric acid of commerce, consisting of about 98 per cent of the acid, the rest being water.

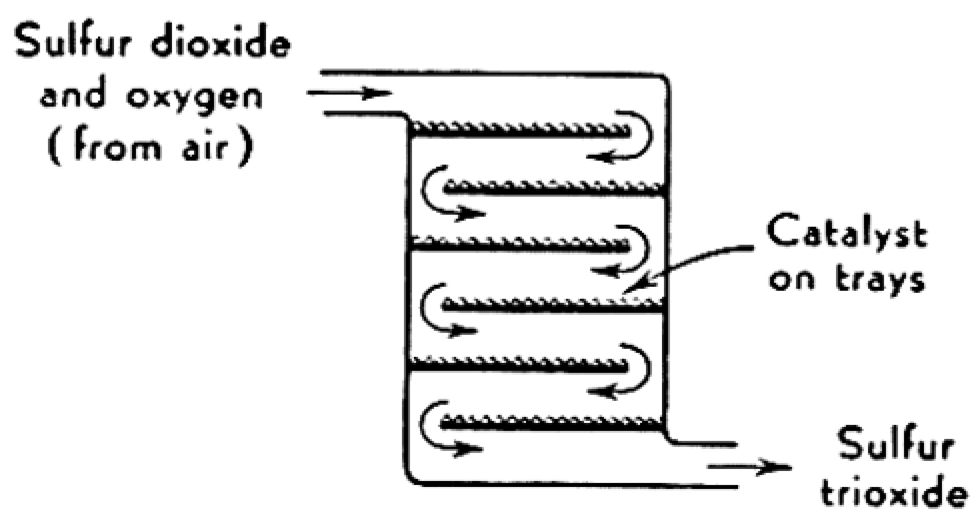


FIG. 37. Essentials of the Contact process.

The sulfur dioxide may be provided by the burning of free sulfur, or it may be taken from the exit gases of smelters which roast metal sulfides; thus this process may be operated in conjunction with a smelter. Because of the possibility of contamination by arsenious oxide (As_2O_3), the sulfur dioxide is passed through flues where this and other solid impurities may settle out. On its way to the contact tower, sulfur dioxide picks up air to supply the requisite oxygen. The mixed gases are washed free of dust and of any residual arsenious oxide by a water spray. They are then dried by sulfuric acid before entering the contact tower. In this tower (see Fig. 37) the gases pass over trays holding the catalyst—platinized asbestos—and conversion to sulfur trioxide is effected.

The equation for the essential reaction involved here is

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 41{,}800 \text{ calories} \quad (58)$$

This is an exothermal reaction and is reversible; and the conditions under which it operates to advantage must be determined in the

light of Le Châtelier's principle (§ 153). The best temperature is found to be about 400°C.

The gaseous sulfur trioxide is next passed into concentrated sulfuric acid, where it is absorbed to form fuming sulfuric acid, commonly known as *oleum*,

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \tag{59}$$

nitrogen and other gases going out into the atmosphere. This oleum may be shipped in suitable containers or first diluted to ordinary concentrated sulfuric acid:

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 \tag{60}$$

Sulfur trioxide is so slowly soluble in water and generates so much heat on solution that it is found preferable to dissolve it in sulfuric acid.

The heat produced in the contact tower is utilized to heat the oncoming gases, thus effecting a saving in fuel consumption. Much of this process is automatic, particularly where electrical energy is available. The chief advantage of this process lies in the high concentration of the acid. But a disadvantage is the liability of the platinum to poisoning by traces of arsenic or mercury compounds. For this reason two substitutes, ferric oxide (Fe_2O_3) and vanadium pentoxide, (V_2O_5), have been used recently. They are cheaper than platinum and not so subject to poisoning.

At the present time over one quarter of all the sulfuric acid produced on this continent goes into the manufacture of fertilizers, most of the remainder being approximately evenly divided among the chemical, metallurgical and petroleum industries.

144 Properties of Sulfuric Acid

This acid is an oily liquid and colorless, unless contaminated with organic matter, when it turns brown or black. It dissolves readily in water with the evolution of a large quantity of heat. Indeed so great is its affinity for water that it is a useful (though frequently destructive) dehydrating agent. In practice the acid is added to water, not water to acid, in order to effect safe dilution. Sulfuric acid acts in the following ways.

(1) *As an acid.* It is in dilute solution that it is characteristically acidic:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow \tag{61}$$

Thus its hydrogen is replaced by the metal zinc forming zinc sulfate.

(2) *As a dehydrating agent.* Here its action falls into one of two classes, the concentrated acid being employed in each instance:

(*a*) Removing free water, as in the drying of moist gases.
(*b*) Removing the elements of water from a compound which contains no water either free or as water of crystallization, but does contain the elements hydrogen and oxygen in such proportion as will produce water. Thus pure cane sugar has all its hydrogen and oxygen removed to leave pure carbon:

$$C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow H_2SO_4 \cdot 11H_2O + 12C \qquad (62)$$

145 Review of Definitions

A reducing agent is the antithesis of an oxidizing agent, that is, it can take up oxygen, for example, sulfur dioxide.

A dehydrating agent is a substance which can remove water (or the elements of water) from a substance containing water (or its elements).

146 Summary

Sulfur is an element which occurs free in nature. It displays allotropy. Its allotropic modifications are of two kinds, crystalline and amorphous. These modifications are easily interconverted.

Hydrogen sulfide is a gas which gives rise to many sulfides in combination with metals.

Sulfur burns in air or oxygen to produce sulfur dioxide (SO_2). It may be further oxidized to sulfur trioxide (SO_3), using air (or oxygen) and a catalyst.

Sulfur dioxide is soluble in water and produces sulfurous acid (H_2SO_3); sulfur trioxide, similarly, with water forms sulfuric acid (H_2SO_4).

When diluted with water, sulfuric acid may react with metals and give hydrogen. But in the absence of water it acts as a dehydrating agent, removing water or the elements of water from other compounds.

Sulfuric acid is manufactured by the Contact process, a very efficient catalytic process.

Questions

1. What is the common source of sulfur, and how may it be obtained therefrom?
2. Compare the properties of a large diamond with those of a piece of charcoal of the same size. Compare the properties of rhombic and plastic sulfur.
3. Compare, in tabular form, the preparation and properties of carbon dioxide and sulfur dioxide.
4. How may sulfuric acid act as (*a*) an acid and (*b*) a dehydrating agent?
5. Describe the manufacture of sulfuric acid.

12

What Is a Chemical Reaction?

147 Characteristics of Chemical Reactions

We have now accumulated sufficient data on what substances may react together and on the nature of their products to review the general considerations involved. These considerations may be stated in this way. (1) The physical properties of the product of a chemical reaction will frequently differ from those of the initial reagents. (2) The chemical properties of the product of a reaction will be different from those of the reagents producing such a reaction. (3) A transfer of energy is involved in every chemical reaction—this is the final criterion. Now between certain elements and under the right stimulus a reaction will occur with violence, for example, between hydrogen and oxygen and phosphorus and bromine; whereas in other instances a reaction may be so slow as to be scarcely measurable with time, such as the union of oxygen and sulfur dioxide in the absence of a catalyst. In still other cases, no reaction may be either measurable or possible. Some substances may be mixed together to give a result physically different, but the components of the mixture may still retain their separate chemical properties. Examples of this class are some common metallic alloys. Solid sodium and solid potassium melted together in about equal proportions give rise to a mixture which is a liquid at ordinary temperatures, but the chemical reactions are those of sodium and of potassium in the proportions in which they are present. An alloy of lead, tin and bismuth may have such a low melting point that it becomes a useful material, in electrical fuses, for example. But there is little evidence to show that these alloys are strictly chemical compounds. Many examples may be provided to show that elements in the same periodic group do not usually combine, whereas the elements of widely separated

groups form very stable compounds with the release of much energy. Sodium and chlorine are examples.

It appears, then, that there must be some disposition on the part of elements to unite before union can ensue; this is the old idea of chemical affinity. On the other hand, some substances form no compounds at ordinary temperatures, but unite at much lower temperatures, only to dissociate again on being heated.

148 Simple Gas Reactions

Much may be learned from a study of reactions among gases where the molecules are free to move and where their speed of motion is determined by the temperature to which they are subjected. This may be visualized in the following manner. Two gases, A and B, are mixed together in a container of fixed volume. Their chance collisions at 0°C may involve the addition of some molecules of A to molecules of B to form molecules of the compound AB. These collisions, however, may not be effective in every instance. A glancing blow may be struck, whereupon they bound away from each other, whereas a head-on collision may conceivably produce a stable molecule of AB. Any energy liberated in this union (an exothermal reaction) may be passed on to adjacent molecules or lost by radiation away from the container. And so eventually, with the numbers of A and B molecules getting fewer and fewer as time goes on, the rate of union slows down. Should heat be added to the mixture, the increased energy of the molecules of A and B appears in their increased rate of travel, thereby enhancing the chances of effective collision. A similar result would be obtained by bringing all the molecules closer together by decreasing the total volume of the container—in the molecules of gases by compression, as Boyle's law indicates. This is tantamount to increasing the concentration of A and B.

149 Reversibility in Reactions

We have previously suggested that in all molecules the atoms composing them are in a constant state of vibration, however limited its amplitude may be. Under such circumstances the heat added to cause A and B molecules to collide effectively with greater frequency may actually cause the atoms of A and B in the compound AB to vibrate so rapidly as to prevent a stabler union's being effected. It is, therefore, conceivable that a temperature

may be reached where the heat required to cause combination actually undoes this combination at the same rate at which it effects it. This condition does not seem to be so disastrous at first sight, however, if C and D will not unite unless they absorb heat (an endothermal reaction, as it is called).

150 An Exothermal Reaction

An interesting example of the first case is given by nitrogen and hydrogen, which will unite to give ammonia according to the equation:

$$N_2 + 3H_2 \rightarrow 2NH_3 + \text{Heat} \tag{63}$$

A mixture of these two gases actually requires considerable heat to bring about union, that is, to effect such collisions of nitrogen and hydrogen molecules as to split, and subsequently reorientate, the atoms into the new arrangement that is ammonia. But the time comes when the heat added, aided by the heat of reaction evolved, decomposes the ammonia as fast as it is formed. Such a condition, called *chemical equilibrium*, is represented by the equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{Heat} \tag{64}$$

In practice this reaction involves a compromise between the temperature required to bring about union and that which defeats this purpose by decomposition of the product.

151 An Endothermal Reaction

A somewhat similar case is the union of nitrogen and oxygen to produce nitric oxide:

$$\text{Energy} + N_2 + O_2 \rightarrow 2NO \tag{65}$$

This is an endothermal reaction, and the addition of heat is effected by the electric arc, which provides a temperature of 3000°C. Theoretically everything is in favor of this reaction—the heat to cause rapid, effective collisions of nitrogen and oxygen molecules, and the heat that must be put into this pair of elements to produce the oxide. But nitric oxide is easily decomposed by the very temperature or degree of heat required to produce it. Again an equilibrium results, which may be advantageously upset, however, by rapidly cooling the mixture after exposure to the arc, catching what nitric oxide has been formed and getting it out of the way before it starts to revert to its elements.

152 Chemical Stability

The above considerations suggest that a chemical compound may have a life of varying duration. This is indeed the case; and any compound which appears to remain indefinitely at ordinary temperatures is termed *stable*, whereas those compounds which revert to their previous condition are termed *unstable*. An unstable compound, therefore, is one with so much internal energy in its atoms that it is seeking a more favorable (stable) arrangement of its component atoms. But the question, then, is bound to arise: "For how long must atoms remain joined together in order that their union may be called a compound?" And also: "How does a compound of short life differ from a mechanical mixture?" The answer to the latter question is obviously that the length of life constitutes the difference; and the answer to the former question can be given only arbitrarily. It is: "Long enough for the observer to be able to demonstrate that its physical and chemical properties differ from those of the initial reagents."

The chances of collision of molecules to form a new compound (or compounds) are much better if only two such molecules are concerned than if three or more are involved. From the atomic chaos at first resulting from an effective collision of molecules, that compound (or group of compounds) results which is most satisfactory to the transfer of energy involved under the specific circumstances of the experiment.

153 Le Châtelier's Principle

An excellent guide to the effect upon a reaction at equilibrium of the application of such factors as temperature, pressure, etc., is given by Le Châtelier's principle, which states, in effect, that a force applied to a reaction at equilibrium causes that equilibrium to shift in the direction of the applied force. Thus, if nitrogen and hydrogen combine to produce ammonia with the evolution of heat (equation 64), added heat will push the equilibrium in the direction of more hydrogen and nitrogen and less ammonia. And if nitrogen and oxygen require heat added to them in order to combine (equation 65), the more heat added the better the production of nitric oxide. But, as shown above, it is frequently necessary to effect a compromise with this principle because of other factors which may be specific in each case.

Two types of reaction have been mentioned above with relation to the direction in which heat is utilized; they are exothermal and endothermal. These are really different ways of looking at the same condition; for example, if

$$N_2 + 3H_2 \rightarrow 2NH_3 + \text{Heat} \tag{66}$$

is regarded as an exothermal reaction, its reversal

$$\text{Heat} + 2NH_3 \rightarrow N_2 + 3H_2 \tag{67}$$

is obviously endothermal. Of these two types, however, the exothermal ones are commoner because they are obviously easier to produce, and, if industrial processes, they are cheaper. Examples of exothermal reactions are the combustion of carbon, hydrogen, sulfur, etc., in air. An outstanding endothermal reaction is the large-scale production of calcium carbide from lime and coke by means of electrical energy at a very high temperature.

154 Heat of Reaction

The amount of heat, measured in calories, which is involved in a chemical reaction is determined by (1) what substances are reacting and (2) what amounts of these substances are reacting. For example, when hydrogen and oxygen unite, however slowly or swiftly, the heat involved is in accord with the equation:

$$2H_2 + O_2 \rightarrow 2H_2O + 116{,}800 \text{ calories} \tag{68}$$

where 4 grams of hydrogen and 32 grams of oxygen unite to produce 36 grams of water and a quantity of heat equal to 116,800 calories. Similarly,

$$C + O_2 \rightarrow CO_2 + 96{,}820 \text{ calories} \tag{69}$$

that is, 12 grams of carbon unite with 32 grams of oxygen to produce 44 grams of carbon dioxide and 96,820 calories of heat. Both these reactions are exothermal, and the heat evolved is definitely one of the products of the reaction. And since energy cannot be created or destroyed, energy equal to 116,800 calories is required to decompose 36 grams of water into hydrogen and oxygen; and energy equal to 96,820 calories is necessary to decompose 44 grams of carbon dioxide into pure carbon and oxygen.

155 Reactions between Gases and Liquids

In order that a gas may react with a liquid it is necessary that they be mutually soluble; otherwise no molecular collisions are

possible. Where a gas is soluble in a liquid and a reaction is possible, the effect of increased temperature is usually such as to render the gas less soluble and so detrimental to production of a compound. On the other hand, the effect of pressure is to force more of the gas into the liquid, making more collisions possible and thereby enhancing the rate of chemical reaction. These statements are in accord with the rules of solubility of gases given in § 163. An example of this type is the solution of ammonia in water. This gas is very soluble at ordinary temperatures and pressures to form a solution (a mechanical mixture). A small quantity of the dissolved ammonia, however, will react with some of the water to produce the rather unstable compound ammonium hydroxide (NH_4OH), as shown here.

$$\underset{\text{Gas}}{\overset{(1)}{NH_3}} + \underset{\text{Liquid}}{H_2O} \rightleftharpoons \underset{\text{Aqueous solution}}{\overset{(2)}{NH_3 \cdot H_2O}} \rightleftharpoons \underset{\text{Ammonium hydroxide}}{\overset{(3)}{NH_4OH}} \qquad (70)$$

An increase of pressure in (1) will force a larger amount of ammonia into the solution to increase (2), which in turn will produce more (3); whereas a decrease in pressure or an increase in temperature will have the reverse effect, and will result in the expulsion of gas from solution. Similar conditions apply to aqueous solutions of carbon dioxide and sulfur dioxide, which contain measurable quantities of carbonic and sulfurous acids, respectively.

156 Solution, an Ideal Reaction Medium

A liquid presents an ideal medium for chemical action because of its compactness of volume in contrast to the gaseous state, and also because of the mobility which molecules of both solute and solvent possess in solution. Water is by far the best solvent. In addition to dissolving the greatest variety of chemical substances, water permits of the formation of ions (§ 178), which, under the stimulus of the electric current, will travel in accord with the laws governing electric circuits. Thus the vast majority of chemical reactions are performed in water. For a great proportion of carbon compounds water is unsuitable, for it scarcely dissolves at all such bodies as gasoline, kerosene, benzene, fats and oils. For them we have far more suitable solvents, such as chloroform and ether, which, however, are non-ionizing solvents.

One advantage of carrying on reactions in a liquid solvent is that, by varying the amounts of reagents used in proportion to the amount of solvent, rapid reactions may be slowed down by dilution, and insoluble products may be precipitated out—in other words, the reaction may be easily controlled. A good example of this control is the reaction between sulfur dioxide and iodic acid (HIO_3). Under suitable conditions the two compounds produce free iodine, which in the presence of starch gives rise to a blue-to-black coloration. If a mixture of water, sulfur dioxide and starch is made in one beaker, and a mixture of water and iodic acid in another, and if one solution is added to the other, the final mixture will turn deep blue after a time interval which depends on two factors: (1) the concentration of the reagents and (2) the temperature of the mixture. If the solutions are warmed prior to mixing, the blue color will appear more quickly after mixing, and the same increase in velocity is observed if the quantities of solutes are increased. This is a simple but dramatic way of showing the effects of temperature and concentration on a reaction.

157 Reaction between Solids

Perfectly dry solids usually show no inclination to react since it is very difficult to reduce them to a sufficiently fine state of division so that their molecules can come within striking distance of one another. For this reason it is obviously preferable to dissolve them in some solvent which will permit them to exist in molecular or ionic form. But at high temperatures, at which the vapor pressure of solids can be appreciable or they tend to liquefy, chemical reaction between solids becomes more feasible.

158 Some Heats of Reaction

Below is a set of chemical equations showing the heats involved in some common chemical reactions, where the number of calories given corresponds to quantities of the reagents in gram-atomic weights:

$$\text{(1)}\ 2H_2 + O_2 \rightarrow 2H_2O + 116{,}800 \text{ calories} \tag{71}$$

$$\text{(2)}\ H_2 + Cl_2 \rightarrow 2HCl + 44{,}000 \text{ calories} \tag{72}$$

$$\text{(3)}\ CaO + 3C + 121{,}000 \text{ calories} \rightarrow CaC_2 + CO \tag{73}$$

$$\text{(4)}\ 2C + O_2 \rightarrow 2CO + 58{,}000 \text{ calories} \tag{74}$$

(5) $C + O_2 \rightarrow CO_2 + 96{,}820$ calories (75)

(6) $3O_2 + 61{,}400$ calories $\rightarrow 2O_3$ (76)

(7) $N_2 + 3H_2 \rightarrow 2NH_3 + 24{,}400$ calories (77)

(8) $N_2 + O_2 + 43{,}200$ calories $\rightarrow 2NO$ (78)

The first equation above indicates that 4 grams of hydrogen unite with 32 grams of oxygen to produce 36 grams of water and give out 116,800 calories. Similarly, the third equation states that 56.1 grams of lime will unite with 36 grams of carbon and absorb 121,000 calories in order to produce 64.1 grams of calcium carbide and 28 grams of carbon monoxide.

159 Summary

A chemical reaction involves a change in physical and chemical properties. The major change involved concerns energy. Without energy no change appears possible.

A reaction which goes on accompanied by an evolution of energy—usually as heat—is known as exothermal. This is the common type of reaction, whereas the less common is that in which energy of some kind must be added before the reaction will proceed—the endothermal type.

Many factors enter into the working of a reaction—the reagents themselves, their physical condition, the type of reaction (endothermal or exothermal), the volume of the products, the presence of a catalyst and the temperature.

Le Châtelier's principle is a useful guide in assessing the behavior of substances in equilibrium, since it states that, when a force is applied to a system in equilibrium, the system reacts to diminish the applied force or to nullify its effects.

Chemical equilibrium results in a reaction that is easily reversible, if the products of the reaction are not allowed to escape. Equilibrium is not a condition of rest but of equally balanced and opposite tendencies.

All reactions are in theory reversible—and many in practice.

Questions

1. What changes may occur during a chemical reaction?
2. Stress the importance of energy to chemical change.
3. Define and illustrate the terms endothermal and exothermal.
4. Define and illustrate reversible reactions and chemical equilibrium, and show the application of Le Châtelier's principle to such systems.

13

Solutions—Mixtures

160 Mixtures

As we already know, a mixture differs greatly from a chemical compound. Examples of mixtures come easily to mind, such as sand and salt, salt and sulfur, sulfur and charcoal. In every such case we are likely to think—perhaps too quickly—of how each constituent of the mixture is visible to the naked eye or under a microscope. Mixtures are frequently called "mechanical mixtures," that is, they may be thought of as being made "by hand" and separated again in the same way. In such a mixture each of the various constituents can be distinguished separately since each is actually leading a separate existence. A mixture of 2 parts of hydrogen and 1 part of oxygen by volume looks and acts physically like one gas. It is far different from water, although the latter consists of the same volume proportions of the same gases, but in this instance *chemically combined.* The difference between these two (the gas mixture and water) may be illustrated very simply in this way. If an electric spark is passed through the gas mixture, it explodes with the evolution of much heat, and what is left behind is just water. Obviously the mixture of gases contained a large amount of potential energy (chemical) which was set free when chemical combination occurred to give water.

The foregoing is a familiar example of the difference between a mechanical mixture and a chemical compound, our chief criterion of differentiation being the energy set free. But many examples of mixtures are not so obvious as this. Sugar dissolved in water is regained completely as a solid only by getting rid of the water by evaporation; this involves the use of heat, but this heat does not change the chemical nature of the sugar or the water. Another mixture is common salt dissolved in water. True, each may be leading its own separate existence in certain respects; but whereas

neither solid sodium chloride nor pure water will conduct electricity to any appreciable extent, the mixture of the two certainly does—and with strange results. We must therefore conclude that in such a mixture each component has some effect on the other.

The simplest of all mixtures is one like air—a mixture of gases—where each constituent goes about its business to a great extent independently of the others. This is well illustrated by the law of partial pressures, which was enunciated by Dalton: *the partial pressure of each gas in a mixture is proportional to the relative amount (by volume) of that gas present.* This means that, if we have two gases in a vessel, the total pressure on the walls is merely the sum of the pressures that the two gases would exert if each were alone in the same vessel. This sounds, perhaps, obvious at first, but it leads us to believe that under ordinary circumstances the molecules of each gas are so far apart from one another that both sets may intermingle without seriously getting in one another's way. As an example of Dalton's law we can take the case of air which is approximately four-fifths nitrogen and one-fifth oxygen. At normal atmospheric pressure, $\frac{4}{5} \times 760$ mm will be the pressure caused by nitrogen alone (that is, 608 mm). The remaining fifth is caused by oxygen, namely, 152 mm.

161 Types of Solutions

One feature about air, which at first caused it to be thought a compound, is its homogeneity. It "looked" the same always. This is true even if the proportions of its components vary within wide limits. The same is very nearly true of white gold, an alloy of gold and silver. We have a name for such a homogeneous mixture, and that is *solution.* A solution then is a mixture of two or more substances so made as to appear as one substance.[1]

Actually we can have nine types of solutions of two constituents only since we have three states of matter. They are (1) gas in gas, (2) gas in liquid, (3) gas in solid, (4) liquid in gas, (5) liquid in liquid, (6) liquid in solid, (7) solid in gas, (8) solid in liquid and finally (9) solid in solid. Air is a familiar example of (1), and we can neglect it as such since we have said so much about gases in applying Boyle's and Charles's laws, which apply as well to a

[1] The word *homogeneous* means *all of one kind.* To use it for a mixture is not strictly correct, but it is rather clumsy to say "a mixture-which-appears-homogeneous."

mixture of gases as to a single gas. We shall pay most attention to (2), (5) and (8) since they are of greatest importance in chemistry at the moment; (9) will be discussed when we consider alloys later.

162 Limits of Solubility

A solution contains two kinds of constituents: the medium by which the act of solution was achieved, called the solvent, and the dissolved matter, called the solute. It has become the custom to use the word solvent for the larger (in volume) of the two constituents and the word solute for the smaller. For example, in a solution of sodium chloride in water, the water is known as the solvent and the chloride as the solute. This relationship can of course be reversed, as with sodium acetate and water as well as with gases, and some liquids which may form solutions in any proportion. We should, however, not lose sight of the fact that a solution of two substances is a kind of contract between the two where each is responsible for the behavior of the other.

Some substances may mix together in any proportion to form a solution; for example, water and ethyl alcohol; copper and aluminum. Such substances we say are *miscible in all* proportions. On the other hand, some substances will not mix at all, such as oil and water, unless a third component is added which will help to dissolve both of them. But in general there are limits to which one substance can dissolve in another so as to produce a homogeneous result. This limit is termed the *solubility* of one in the other, where the single word solubility means *maximum amount soluble* under certain conditions. Thus sodium chloride will dissolve in 100 grams of water at 0°C to the extent of 35.7 grams; and at 100°C to the extent of 39 grams—and no more. The solubility of sodium chloride is then 35.7 grams at 0°C, and 39 grams at 100°C.

Over the temperature range from 0° to 100° there is thus an increase in solubility of 39 − 35.7, or 3.3 grams. Dividing 3.3 by 100 (the temperature range) we obtain 0.033; this last value is called the *temperature coefficient of solubility* of sodium chloride.

Carbon dioxide gas is soluble in 100 grams of water to the extent of 179.67 ml at 0°C and 90.14 ml at 20°C. There is in this instance a decrease in solubility of 179.67 − 90.14, or 89.53 ml. This value, divided by 20 (the temperature range), gives us −4.477 as the temperature coefficient for carbon dioxide in water.

At the temperature given above, first sodium chloride and then carbon dioxide are shown as having a limit to their ability to dissolve in a known quantity of water. When this condition exists the solution is said to be a *saturated* one. It will be noted that in each of these two cases the saturation is dependent on the temperature. If a quantity of water at 100°C contains sodium chloride from nothing up to, but not reaching, the figure of 39 grams per 100 grams of water, the solution is said to be *unsaturated*; if it contains 35.7 grams per 100 at 100°C it would be unsaturated, although if the temperature was lowered to 0°C it would just become saturated at that point.

163 Gases in Liquids—Type 2

A familiar example of this type of solution is soda water, which is commonly sold in bottles under pressure and consists of a solution of the gas carbon dioxide in water. Experience shows that the release of pressure, by lifting the cap, causes the release of much of the dissolved carbon dioxide; thus pressure influences solubility of a gas in water. Also warm soda water loses its gas—therefore its taste—much more rapidly than cold; hence temperature influences solubility of a gas.

These observations on gas-water solutions suggest the following generalizations.

Nature of the Substances Involved. The solubility of a gas in water varies with different gases, ammonia (NH_3) being very soluble, carbon dioxide fairly so, oxygen to a lesser extent and hydrogen almost insoluble—all being compared under the same conditions of temperature and pressure. Ammonia, though very soluble in water, is much less so in, say, alcohol. In order that two substances may be soluble, one in the other, there must be some kind of mutual attraction between them.

Influence of Pressure. Henry's law. The solubility of a gas in a liquid is proportional to the pressure of the gas. This will recall Boyle's law which shows how the molecules of a gas may be crowded into a smaller volume by the exercise of pressure.

Influence of Temperature. Provided that a gas is at all soluble, the higher the temperature the smaller the quantity of gas dissolved in a given quantity of solvent. Then the best conditions for obtaining a solution containing a large quantity of dissolved gas are high pressure and low temperature.

164 Liquids in Liquids—Type 5

There are three possible combinations here: (*a*) Liquids miscible in all proportions, as ethyl alcohol and water, glycerol and water, benzine and turpentine. (*b*) Liquids that do not mix at all, as gasoline and water. (*c*) Liquids having a partial solubility, each in the other.

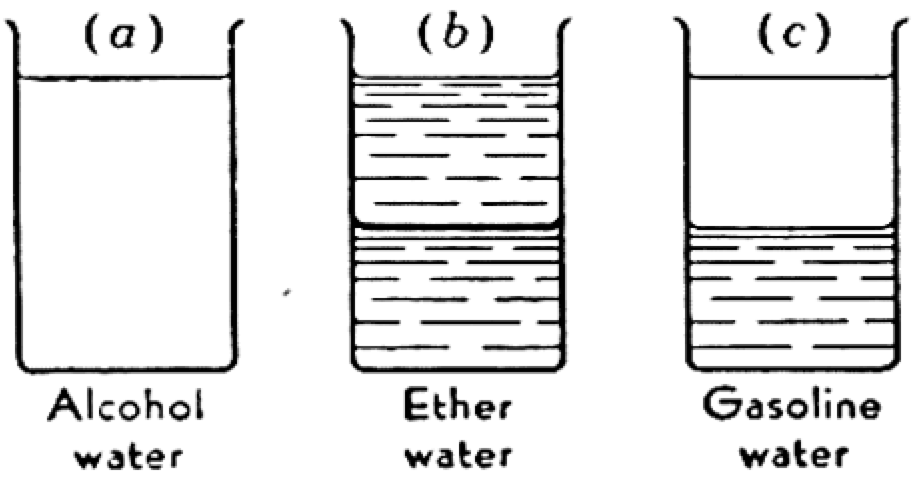


FIG. 38. Illustrating complete miscibility, partial miscibility, and immiscibility of liquids.

A solution such as (*a*) is definitely homogeneous, (*b*) is definitely heterogeneous and (*c*) is both homogeneous and heterogeneous. These three are exemplified in Fig. 38. The first type represents the "true" solution as compared with a suspension (or colloidal) type of solution which shows an opalescence under the influence of light. The immiscible liquids (*c*) may, by the addition of another liquid, sometimes revert to the colloidal type. Examples of (*b*) frequently become homogeneous on raising the temperature, for example, carbolic acid in water.

Solutions composed of liquids only do not conform to such simple laws as govern the behavior of types 2 and 8.

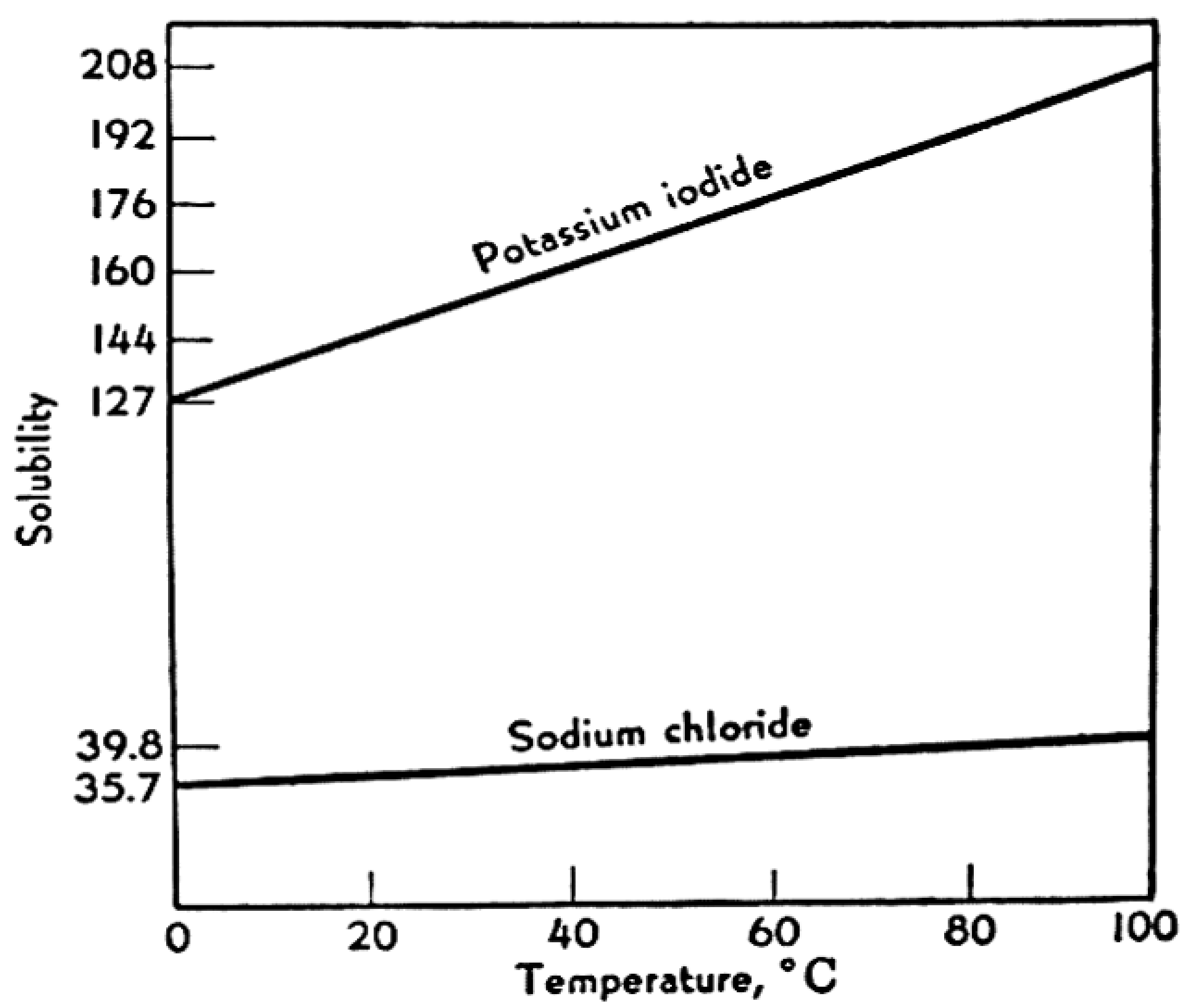


FIG. 39. How the solubility in water of two common inorganic salts changes with temperature. The solubility is expressed as grams of solute per 100 grams of water.

165 Solids in Liquids—Type 8

Like gases, solids vary greatly in their ability to dissolve in the same or different liquids. But in these instances the temperature alone controls the degree of solubility since pressure has a negligible effect. It is a general rule that *solids dissolve in liquids to a greater extent at a high temperature than at a low one.* Figure 39 shows the solubility curves of two common solids in water for various temperatures; the form of the curve indicates how the temperature coefficient will vary for each of the solutes listed.

Of the many solids and liquids available for this study, only a few simple examples will be chosen. In all cases water will be used as the solvent.

SOME PROPERTIES OF AQUEOUS SOLUTIONS

166 Saturation

If a small quantity of crystalline potassium nitrate (KNO_3, saltpeter) is added to a large quantity of water and stirred, the crystals will be seen to disappear and can be identified later in the water; the salt has dissolved. If the temperature of the water is kept at 0°C, from start to finish, we shall find that continued addition (with stirring) of quantities of potassium nitrate will result in more of the solute dissolving until at last no more will dissolve, 13.3 grams per 100 grams of water to be exact (see Fig. 40). At that moment we have crystals of the excess solute surmounted by the clear solution of potassium nitrate in water. When no more will dissolve at this temperature the solution is said to be saturated with potassium nitrate. Before this condition was reached, however, the solution was unsaturated. If the solution is now cooled slightly, some crystals will come out of the solution and be deposited on the bottom of the container, until the solution is again saturated, though the water at this lower temperature holds less solute than at 0°C. On being warmed again, the precipitated solute goes back into solution until the same quantity of nitrate is held in solution as before. Now if warming is continued, more crystals will go into solution. Thus heating causes the solution to become unsaturated, that is, able to hold more solute at the higher temperature. But at, say, 100°C a fixed quantity only of solute (247 grams per 100 grams of water) can be held in solution. Thus saturation must depend upon the temperature; in other

words, the solubility of potassium nitrate will vary directly with the temperature. This, it will be remembered, is the reverse of the statement for a gas-water mixture. This rule holds for nearly all solids which are at all soluble in liquids. Also the degree of solubility brought about by increase in temperature varies just as the individual ability of any solid to dissolve. The application of pressure has so negligible an effect that it may be disregarded in the solid-liquid systems.

A solution which is unsaturated may be made saturated in three ways: (1) by adding more solute, (2) by removing solvent (by dis-

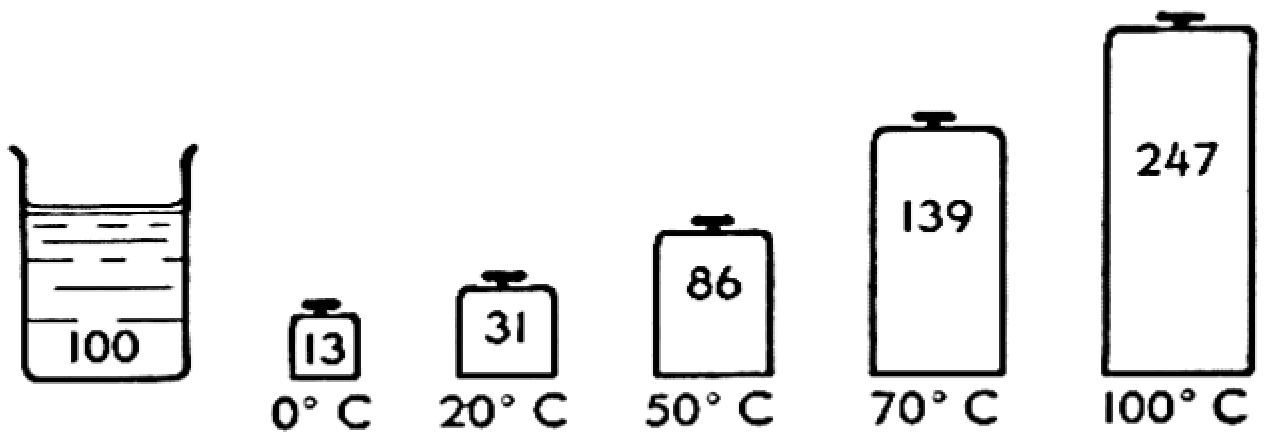


FIG. 40. One hundred grams of water will dissolve an increasing weight of potassium nitrate as the temperature is raised; at each temperature the solution is saturated.

tillation) and (3) by cooling until crystals begin to separate out. Conversely, a saturated solution may readily be made unsaturated (1) by adding more solvent, (2) by cooling to remove crystals of solute and then reheating to its former temperature in the absence of crystals of the solute and (3) by heating to a higher temperature.

167 Supersaturation

There is a curious phenomenon displayed by a few solids and most gases, known as *supersaturation*. We may readily demonstrate this, using sodium thiosulfate ($Na_2S_2O_3$, commonly called photographer's hypo). If a saturated solution of hypo in water is made at about 90°C and carefully filtered at this temperature so as to separate the solution from undissolved crystals, particles of dust, glass, etc., and then allowed to cool slowly down to 20°C without jarring in any way, the excess of crystalline solid that should separate out (that is, the quantity the solvent can hold between 20° and 90°C) will not crystallize out. Such a solution is unstable, for it holds in solution far more solute than it should or could if a crystal of hypo had been present during the cooling process; this is a supersaturated solution. That it is so may be

shown in several ways. Vigorous shaking, or the addition of a piece of solid with a sharp edge, will cause precipitation; if not, then the addition of a crystal of the solute, or of a substance having the same crystalline pattern, will immediately precipitate this excess—so much so that the whole mass may set to a slushy consistency. At the same time it will become warm because the heat liberated is that formerly required to permit this excess hypo to go into solution.

This phenomenon of supersaturation is not frequently met in solid-liquid systems but is very common in gas-liquid systems, and in the latter system steps have to be taken to obviate it—such as rapid mechanical agitation. This effect can be observed with a glass of soda water, where the slow evolution of carbon dioxide may be hastened by shaking or stirring.

The terms saturated, unsaturated and supersaturated, though apparently self-sufficient, must be understood as applying to one solution at one temperature and one pressure only in order to be exact. In addition to these three terms describing solutions there are others in general use, dilute and concentrated. In dilute solutions a relatively small mass of solute is dissolved in a relatively large mass of solvent. This term is very loose; we can easily see that a dilute solution of a very slightly soluble substance might easily be a saturated solution. In a concentrated solution, on the other hand, a relatively large quantity of solute is dissolved by comparison with the mass of solvent. There are also, denoting the chemical rather than the physical content, the more exact terms normal and molar, which are based upon the molecular weight of the solute; and standard, which indicates that the exact content of the solution is known however much or little it may contain.

Percentage is a common method of defining the composition of a solution, but it is not widely used by chemists. A solution of 10 grams of salt dissolved in 90 grams of water, making a total of 100 grams, is called a 10 per cent solution of salt in water.

168 Diffusion in Solution

Solutes diffuse throughout a solvent just as do gas molecules except that their velocity of diffusion is much less. This can be proved by putting a few crystals of potassium permanganate in the bottom of a test tube (see Fig. 41) and carefully covering them

with about 3 inches of water. The test tube is not disturbed throughout the progress of the experiment, and, if a piece of ruled paper is pasted at the back of it, we can observe the deep purple color rising from the bottom and slowly filling the space occupied by the liquid. This simple experiment shows that dissolved molecules, like gas molecules, have a motive power of their own.

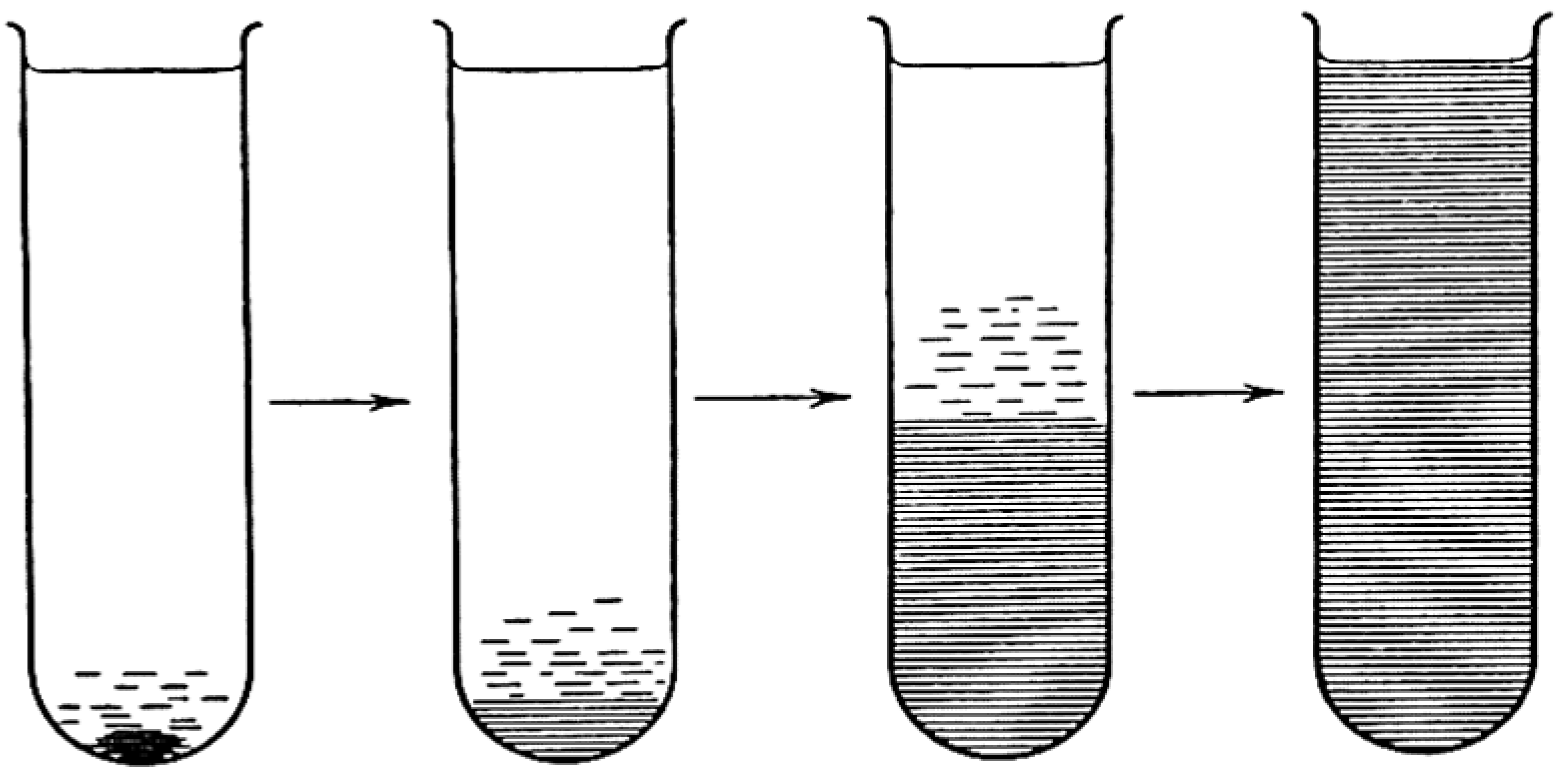


FIG. 41. A crystal of potassium permanganate at the bottom of a test tube of water dissolves and imparts a deep purple color to the solution. This color slowly spreads upwards until the water is of a purple hue. Thus solutes diffuse slowly in a solvent if undisturbed.

169 Vapor Pressure of Solutions

Two test tubes are put in a rack side by side. The first is filled to a short distance from the top with distilled water; the second is

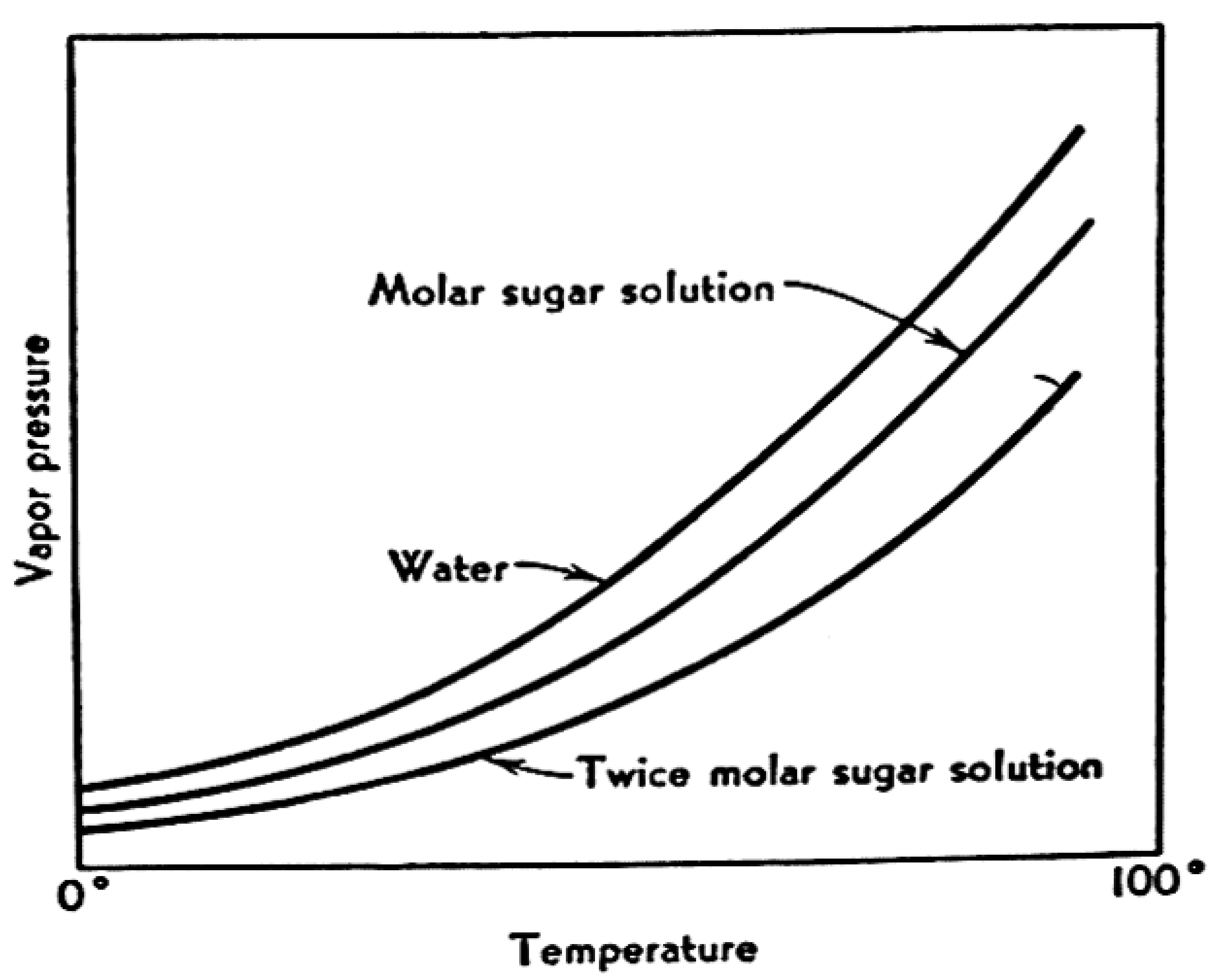


FIG. 42. The vapor pressure curve of a sugar solution always lies below that of pure water.

filled to the same height with a solution of sugar of, say, 10 per cent concentration. The rack is now put in a warm place and left for several hours. At the end of this time the water level will be found to have fallen more than the sugar-water level. This shows very simply that the evolution of water vapor was more rapid from the distilled water than from the sugar-water solution.

Figure 10, on page 28, showed the vapor pressure of water for various temperatures. In Fig. 42 the same curve is repeated and marked "water"; but lying below it are two other curves, one marked molar sugar solution and the other twice molar sugar solution. These curves show that (1) *the vapor pressure of a* sugar *solution is always lower than that of the water itself* and (2) that *the more concentrated the solution the lower the vapor pressure.* In general it may be said that the lowering of the vapor pressure is the same for the same molecular concentration. In other words, the *lowering is dependent on the number of dissolved particles* rather than on the kind of solute.

170 The Freezing Point of a Solution

It is well known that water containing a solute freezes at a lower temperature than water itself; hence the use of salt shaken on frozen sidewalks and steps as well as used with ice to freeze ice cream. It is not so commonly known, however, that the freezing point of a quantity of water may be progressively depressed by the addition of quantities of a solute. This progressive depression was enunciated by Raoult thus: *The gram molecular weight of a substance* [like sugar], *when dissolved in 1000 grams of water, will cause a freezing point depression of 1.86°C.* Since the gram molecular weight is a measure of the number of molecules in that weight, each dissolved molecule contributes its quota to the depression observed. Therefore a fractional or multiple gram molecular weight should produce a

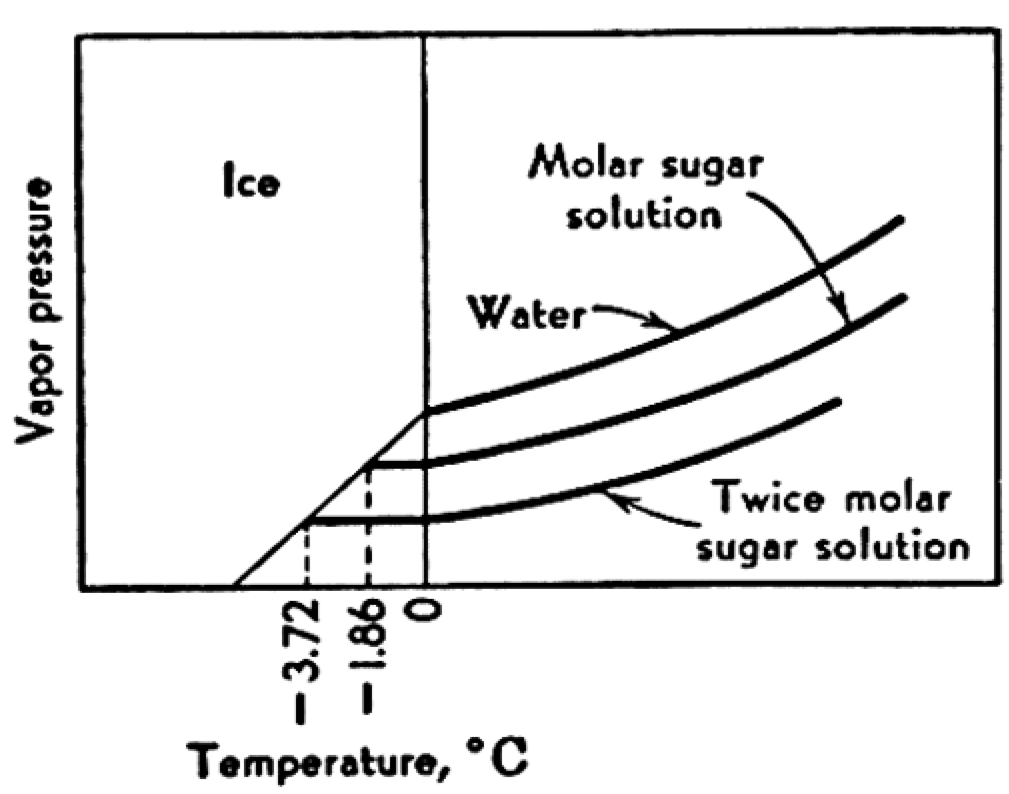


FIG. 43. The vapor pressure curves of solutions of sugar cut the vapor pressure curve of the ice below 0°C. Consequently the freezing points of these solutions are below 0°C.

proportional change in this depression. This is of great theoretical importance; practically, too, it shows how aqueous solutions may be prepared which will not freeze except well below 0°C—the principle of anti-freeze mixtures, for example.

If we extend the curves in Fig. 42 to the left-hand side and enlarge them somewhat we obtain Fig. 43. Here we see how the vapor pressure curve of the molar solution cuts the vapor curve of ice. At this point the vapor pressure of ice is the same for the molar solution, that is, the freezing point of the latter is -1.86°C. Similarly the vapor pressure curve of the twice molar sugar solution cuts the vapor pressure curve of ice at -3.72°C, that is, 2×1.86°C. From the above it is possible to calculate what will be the freezing point depression (below 0°C) for a substance like sugar from the formula

$$\Delta \text{ Freezing point} = 1.86 \times \frac{W}{M} \times \frac{1000}{w}$$

where Δ is the depression, M is the gram molecular weight, W is weight in grams of solute and w is weight in grams of water. The molar freezing point depression for water is 1.86, the corresponding figure for acetic acid is 3.9 and for benzene 5.12.

171 The Boiling Point of a Solution

When the atmospheric pressure registers 760 mm of mercury, pure water boils steadily at a fixed temperature, 100°C, for this is the temperature at which water has a vapor pressure equal to the pressure of the atmosphere. If to the boiling water a little sugar is added, ebullition ceases for a while. If heating is continued, it is resumed; but the temperature now is higher than before. That is, the addition of sugar definitely lowers the vapor pressure of the water, and that pressure of 760 mm can be attained only at a higher temperature, that is, above 100°C. Also, the more sugar dissolved, the higher becomes the boiling temperature of the solution. As before, each molecule of the solute contributes to the lowering of the vapor pressure of the water and hence to the elevation of the boiling point.

In Fig. 43 neither of the vapor pressure curves for the sugar solutions had reached the 760 mm point when the temperature had reached 100°C; that is, these solutions do not boil at this temperature. But, proceeding as in the previous section, we may

enlarge the right-hand side of Fig. 43 to obtain the following (Fig. 44). The vapor pressure of the molar sugar solution continues to increase until it reaches the 760 mm line, where it reaches the atmospheric pressure and boiling ensues. The temperature has now reached 100.52°C, that is, a boiling point elevation beyond that of water of 0.52°C. Similarly, the vapor pressure curve of twice molar sugar solution cuts the 760 mm line at 101.04°C—a boiling point elevation of 1.04°C, or twice 0.52°C. These results are summarized in the second Raoult law: *The gram molecular weight of a substance* [like sugar] *when dissolved in 1000 grams of water, causes an elevation of the boiling point of 0.52°C.* The molecular elevation for water is thus 0.52; for benzene the value is 2.43, for chloroform 3.41 and for ethyl alcohol 1.14.

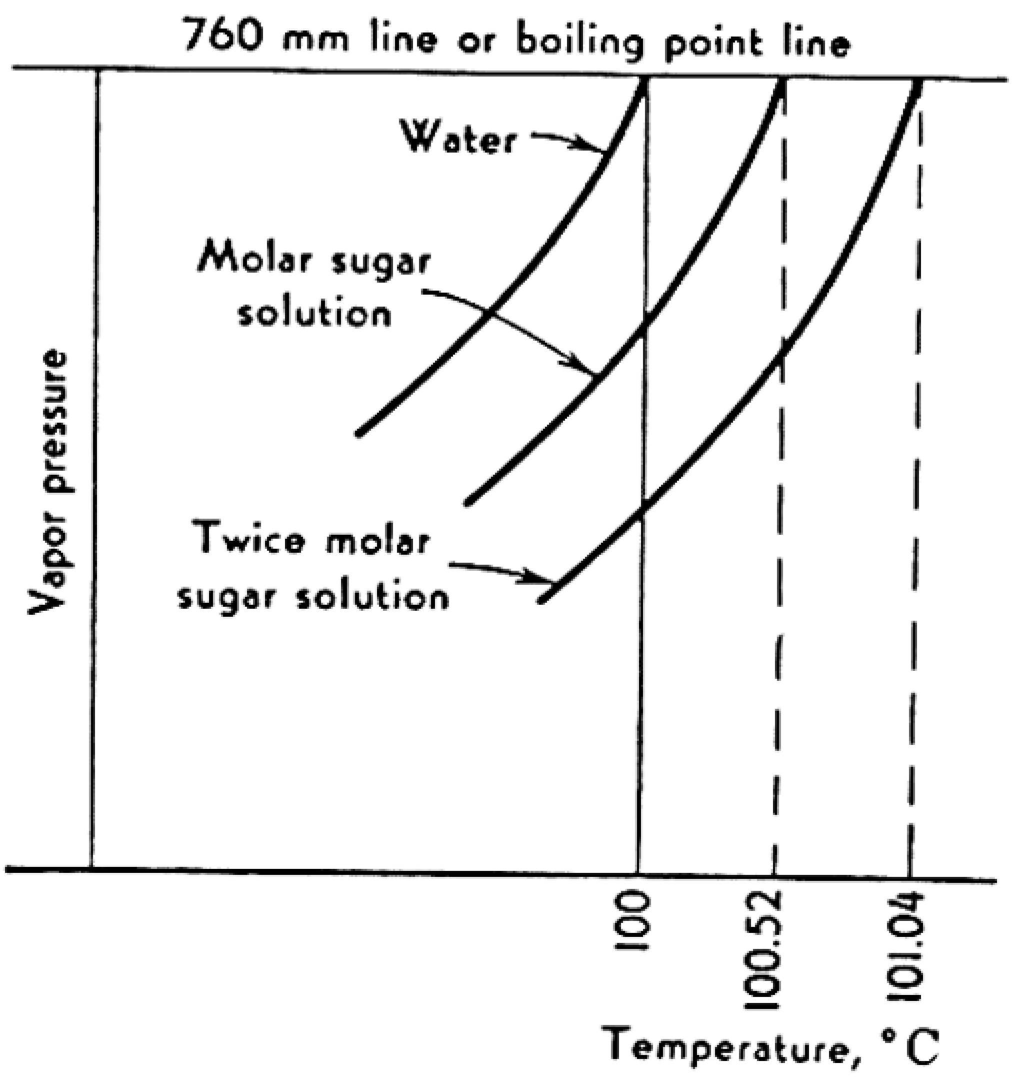


Fig. 44. The vapor pressure curves of solutions lying below that of water cut the boiling point line at points above 100°C; their boiling points are therefore above 100°C.

As for the freezing point, the boiling point elevation of such solutions can be calculated from the formula

$$\Sigma \text{ Boiling point} = 0.52 \times \frac{W}{M} \times \frac{1000}{w}$$

where Σ is elevation, W is weight of solute, M is the gram molecular weight of solute and w is weight of water.

As with vapor pressure and freezing point changes, the elevation of the boiling point is directly dependent on the number of molecules of the solute rather than the nature of the solute.

The foregoing considerations have many common, daily applications. An "anti-freeze" solution is, or may be, depending on the solute selected, an "anti-boil" solution. A "charged" car battery will not freeze in winter. A sugar solution ready for candy making can produce a bad burn when spilled on the skin. Concentrated solutions of common salt or of calcium chloride are useful in the rapid freezing of foods.

The theoretical importance of these considerations is that a close relationship exists between the vapor pressure of a liquid, on the one hand, and the depression of the freezing point and the elevation of the boiling point of the same liquid on the other.

172 Osmosis

A solution enclosed within an animal membrane, which in turn is immersed in the pure solvent, will gradually increase in volume, probably causing the container to burst from the entry of the solvent through the membrane walls. This may be demonstrated in a more practical manner (Fig. 45). A long thistle funnel, open at both ends, has the larger end covered tightly by some suitable tissue such as parchment paper. It is fixed vertically, parchment end downwards, so that it dips into a large reservoir of water. Into the inverted funnel is poured a little water containing sugar so that the level of the solution inside the funnel is the same as that of the pure water outside. This solution is left for several hours. After a while the level of the solution within the tube has risen considerably, water entering through the parchment covering at the expense of the water in the outer reservoir. A test will indicate that no sugar has passed from the inside to the pure water on the outside. After several hours more, the height of the liquid in the funnel will become constant, probably having a height of several feet above the level of the water in the reservoir. But this height of solution exerts a definite pressure of its own, called hydrostatic pressure, on the parchment covering at the bottom.

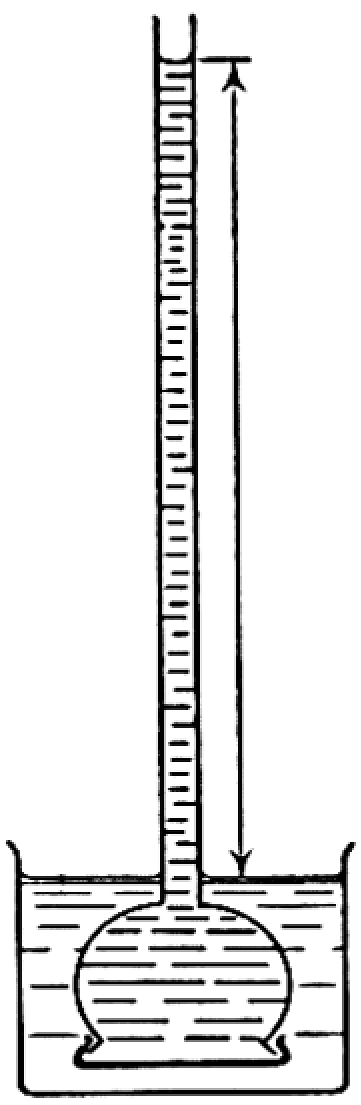


FIG. 45. *Osmosis.* Water enters through a semipermeable membrane to dilute a solution inside, and pressure is developed within.

The covering is obviously selective since it lets water in but does not let the sugar out. It has been called, in consequence, a *semipermeable membrane.* The phenomenon of the passage of the liquid through from solvent to solution is called *osmosis,* and the pressure exerted by the solute (in this case sugar) causing this flow of liquid upward is called osmotic pressure. Since this pressure reaches its maximum at its maximum elevation above the water in the reservoir, it equals the hydrostatic pressure of the column of liquid it produces. This hydrostatic pressure can easily be meas-

ured (32 feet of water = 760 mm of mercury = 14.5 pounds per square inch).

To secure satisfactory quantitative results, the temperature throughout the experiment must be maintained, the barometric pressure should not change, the concentration of the solution originally placed inside the membrane should be known and the membrane should not leak. (A freshly dug carrot, with its tendrils attached, and partially hollowed out, makes a good cell.)

This phenomenon of osmosis, for which we are indebted to Pfeffer the botanist, has been intensively studied. The relationships of concentration, temperature and pressure are expressed in the following statement: *The gram molecular weight of a substance* [like sugar], *when dissolved in 22.4 liters of water, causes an osmotic pressure of one atmosphere at 0°C.*

The height mentioned above during the development of pressure is that where the hydrostatic pressure of the column exactly balances the pressure of water driving in through the membrane, that is, the osmotic pressure. As this osmotic pressure changes with concentration, the height changes. A change in temperature likewise changes this height, that is, changes the osmotic pressure. In fact the change is the same as the pressure change with gases, as shown previously under Charles's law, that is, $\frac{1}{273}$ for each rise or fall in temperature from 0°C. In short, the osmotic pressure varies directly as the absolute temperature as long as the solution neither freezes nor approaches the boiling point too closely.

173 Are Solutions Gases?

On page 115 it was stated that the gram molecular weight of a gas occupies a volume of 22.4 liters at a pressure of 1 atmosphere and at 0°C.

A similar statement for aqueous solutions is: The gram molecular weight of a substance dissolved in 22.4 liters of water will develop an osmotic pressure of 1 atmosphere at 0°C. The only real difference between these two statements is that the former refers to gas pressure whereas the latter mentions osmotic pressure. It was van't Hoff who first drew attention to this similarity and, since the gas laws hold well for few gas molecules in much space (a dilute condition), they hold also for dilute solutions. Therefore it appears that a solid solute dissolved in water behaves like a gas in space, that is, like a gas with no water present. This is a very

important statement for we can now apply Avogadro's law to solutions: Equal volumes of all solutions at the same temperature and osmotic pressure contain the same number of solute particles. Solutions showing the same osmotic pressure are called *isotonic.*

In the experiment on osmosis it appeared that the flow of water was from the pure water to the solution, that is, from a solution of zero concentration of solute towards a solution of finite concentration. If the water in the dish had been a $\frac{1}{2}$ per cent sugar solution, the 1 per cent sugar solution in the thistle funnel would still have risen, but it would not have risen so far. Consequently we can say (1) that osmosis will develop if a semi-permeable membrane separates two solutions of different concentration and (2) that no osmotic pressure will be produced by separating two solutions of the same concentration if they are at the same temperature.

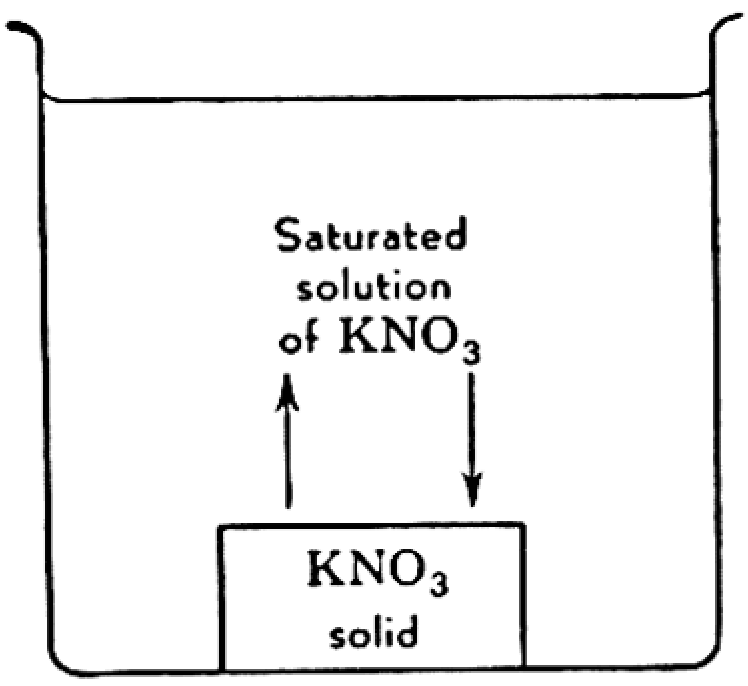


FIG. 46. In a saturated solution of a salt, with undissolved salt present, an equilibrium exists between the undissolved and the dissolved; that is, molecules are going into solution at exactly the same speed that molecules are returning out of solution—as long as the temperature remains constant.

174 Equilibrium in Solution

If we shake up 100 grams of water at 25°C with 50 grams of potassium nitrate most of this salt will dissolve. As long as the temperature remains 25°C, however, about 13 grams will remain undissolved. Is this condition static? If we warm the solution above 25°C, more crystals will dissolve; if we cool the solution below 25°C, some crystals will separate out. From this we conclude that in a saturated solution the condition is not static. This is pictured diagrammatically in Fig. 46, where a lump of potassium nitrate is shown giving molecules to the saturated solution at the same speed as molecules are returning from the solution to deposit as crystals. This is put into equation form as follows:

$$KNO_3 \text{ (undissolved)} \rightleftharpoons KNO_3 \text{ (dissolved)}$$

that is, an equilibrium exists between the undissolved and the dissolved molecules in a saturated solution of the solid. This equilibrium is upset by a change in temperature in accordance

with Le Châtelier's principle, which states that, when to a system in equilibrium a force is applied, the system reacts so as to diminish the applied force.

That this idea of physical equilibrium in solution is not imaginary is shown when very fine crystals, left in contact with their saturated solution, show a diminution in number but an increase in size. Thus small crystals with a large total surface (with a large surface energy) go into solution to form large crystals with a smaller total surface and hence a smaller surface energy. This phenomenon is of considerable value in quantitative analysis, for a precipitate so fine as to run through a filter paper may grow on standing to larger particles which may be filtered without loss.

175 Review of Definitions

A solution is a homogeneous mixture of two or more constituents.

A "true" solution shows no opalescence or turbidity when viewed in a strong light.

Dalton's law of partial pressures is that the partial pressure of any gas in a mixture is proportional to the relative amount (by volume) of that gas present.

Solubility (used exactly) is the maximum amount of a solute which can be dissolved in a fixed amount of solvent at fixed temperature and pressure.

The temperature coefficient of solubility is the amount by which a solute varies in solubility for each 1°C change in temperature.

Henry's law (for gases) is that the solubility of a gas in a liquid is proportional to the pressure of the gas (at some one temperature, of course).

A dilute solution is one which contains a relatively small amount of solute; a concentrated solution is one which contains a relatively large amount of solute, in a fixed quantity of solvent.

A saturated solution is one which contains all the solute possible at that temperature and pressure.

An unsaturated solution is one which contains less than that required for saturation.

A supersaturated solution is one which has been coerced into containing more solute than is required for saturation.

A molar solution is one which contains the gram molecular weight of solute in 1000 ml of total solution.

A normal solution is one which contains the gram equivalent weight of solute in 1000 ml of total solution.

A standard solution is one whose content of solute is accurately known.

Raoult's laws are: (1) The gram molecular weight of a substance dissolved in 1000 grams of water causes a freezing point depression of 1.86°C. (2) The gram molecular weight of a substance dissolved in 1000 grams of water causes a boiling point elevation of 0.52°C. These laws hold for non-electrolytes only.

Osmosis is the selective passage of a solvent through a membrane accompanied by an increase in pressure within the membrane. This pressure is called osmotic pressure. The gram molecular weight of a non-electrolyte dissolved in 22.4 liters of water at 0°C will develop an osmotic pressure of one atmosphere (760 mm Hg).

176 Summary

A solution, which is a homogeneous mixture of two or more substances, is composed of two parts—a solvent and a solute. Although these components may be of any of the three states of matter, the most important are those in which the solvent is water and the solute a gas, a liquid or a solid.

All liquids show the phenomena of vapor pressure, viscosity and surface tension; these properties are dependent on the temperature mainly. But a solute dissolved in a solvent alters the properties of the solvent very considerably.

The solubility of one substance in another (except one gas in another gas) depends on a number of factors. Gases are more soluble in water at a high pressure and low temperature than when the pressure is low and the temperature high. Liquids and solids do not have their solubility influenced by pressure to any marked degree, but are dependent largely on the temperature. Solids are usually more soluble at a high temperature than at low.

For any temperature there is a limit to which a solid or gas may dissolve in water. A saturated solution is one in which the solvent has reached its limit of containing more solute. Below this limiting value solutions are said to be unsaturated; above this limit a few solids (and more gases) may go to form unstable solutions known as supersaturated.

The vapor pressure of a solution is always less than that of the pure solvent at any one temperature; hence the boiling point is always higher.

The freezing point of a solution is always less than that of the pure solvent.

Solutions display osmotic pressure in proportion to the concentration of solute.

Solutes may be classified according to whether they do or do not conduct the electric current when dissolved in water. Those that do not conduct are called non-electrolytes. For non-electrolytes there are definite statements connecting the freezing point, boiling point and osmotic pressure with the concentration of the solution.

Liquids may dissolve in liquids in any proportion or to a limited degree; in the latter instance they form two layers in their container, the less dense floating on top of the more dense.

Raoult's laws summarize the effects of concentration of solute on the freezing and boiling points of a solution (of a non-electrolyte).

Questions

1. Why does water evaporate if left open to the atmosphere? How does this occur? Why does hot water evaporate more rapidly than ice?
2. Compare unsaturated, saturated and supersaturated solutions.

3. What factors influence the solubility of a gas in a liquid? Of a solid in a liquid?
4. How may any two liquids behave when poured into the same container?
5. What do the following words mean when applied to solutions: normal, molar, dilute, concentrated, standard?
6. Describe by a diagram how osmotic pressure may be demonstrated. Why are temperature and hydrostatic pressure important in this phenomenon?
7. Define solubility, temperature coefficient, homogeneous, heterogeneous, vapor pressure, semi-permeable, equilibrium.

14

Acids, Bases, Salts

177 Electrolytes

In the preceding chapter we have stressed the fact that the quantitative rules respecting vapor pressure, freezing point depression, boiling point elevation and osmotic pressure of aqueous solutions apply to what we have called "sugar-like" substances which represent by far the majority of known chemical compounds. Water is not the only solvent to which these rules apply; for just so long as we know the molar depression or molar elevation, for example, so long do we find these rules to hold. But, just as we have seen that the gas laws show deviations at high pressures and low temperatures (that is, at high concentrations of molecules), so we find solutions wavering in their obedience to these rules when the molecules tend to pack closely together. In other words, the condition of the dissolved particles introduces a complication.

We now come to two classes of compounds which show a distinctly abnormal behavior in solution with respect to their vapor pressure, freezing point, boiling point and osmotic pressure. The second of these two classes will be treated later under the heading of colloids; the first consists of acids, bases and salts and will be studied now. This class consists largely of inorganic compounds, which, although not the most numerous in the whole of chemistry, are the most important in that branch of the subject which most concerns us at the moment—inorganic chemistry.

The aqueous solutions of acids, bases and salts do not differ much in appearance from solutions of other substances, unless it happens that they are colored. But one striking difference is that they conduct the electric current, whereas solutions of sugar, alcohol, etc., do not. For this reason we call acids, bases and salts *electrolytes;* by contrast sugar, alcohol, etc., are known as *non-elec-*

trolytes. We can now see that our rules, previously developed in this paper, apply to non-electrolytes. We therefore have to consider the less numerous but highly important electrolytes. They must be defined as those compounds which, when dissolved in water, will conduct the electric current. It must be noted here that, although some other solvents help to bring this about, they are not very numerous, not so efficient and not so easy to use. Under the terms of this definition, an electrolyte is not obliged to conduct electricity when pure. Hydrochloric acid is an acid, when it is an aqueous solution of the gas hydrogen chloride. In the dry state it does not conduct electricity. Pure, dry, solid sodium hydroxide will not conduct electricity either, although when dissolved in water the solution is an excellent conductor. In the same way, sodium chloride, the salt of these two compounds, does not in the pure crystalline state conduct electricity, although its aqueous solution is used industrially to produce chlorine by electrolysis.

Sometimes a certain amount of confusion exists about the term *base.* Let us here define a base as *any substance which can be made to neutralize an acid.* Sodium, potassium and calcium hydroxides will dissolve in water and are neutralized rapidly. Magnesium oxide (MgO), manganese oxide (MnO) and ferrous oxide (FeO) are examples of bases which may need prolonged treatment to neutralize the acid because they are relatively insoluble in water. In such circumstances the word "base" in the phrase "acids, bases and salts" commonly means soluble bases such as sodium, potassium and calcium hydroxides—the same substances which we commonly call alkalies. In what follows, therefore, we shall mean "alkalies" whenever we use the older term "base."

178 Properties of Electrolytes

Here we can do no better than refer to Figs. 42, 43 and 44, where we showed the effect of a non-electrolyte (sugar) on the vapor pressure of water. In Fig. 47 a comparison is made among water, molar sugar solution and molar sodium chloride solution. This figure is purposely drawn out of proportion so that all the important facts may appear together. Here it is apparent that the molar sodium chloride solution curve, between 0° and 100°, lies below even that of the molar sugar solution. Since we are justified in expecting the gram molecular weight of sodium chloride to

contain the same number of molecules as the gram molecular weight of cane sugar (6×10^{23}, Avogadro's number), the action of sodium chloride is abnormal. Indeed, judging from the distance of each of these curves from that of pure water, the sodium chloride seems to have lowered the vapor pressure twice as much as did the corresponding molecular quantity of sugar. Generally, then, we may say that *the vapor pressure of an aqueous solution of an electrolyte is always lower than that of a non-electrolyte of comparable concentration,* that is, abnormally low. It looks, therefore, as if

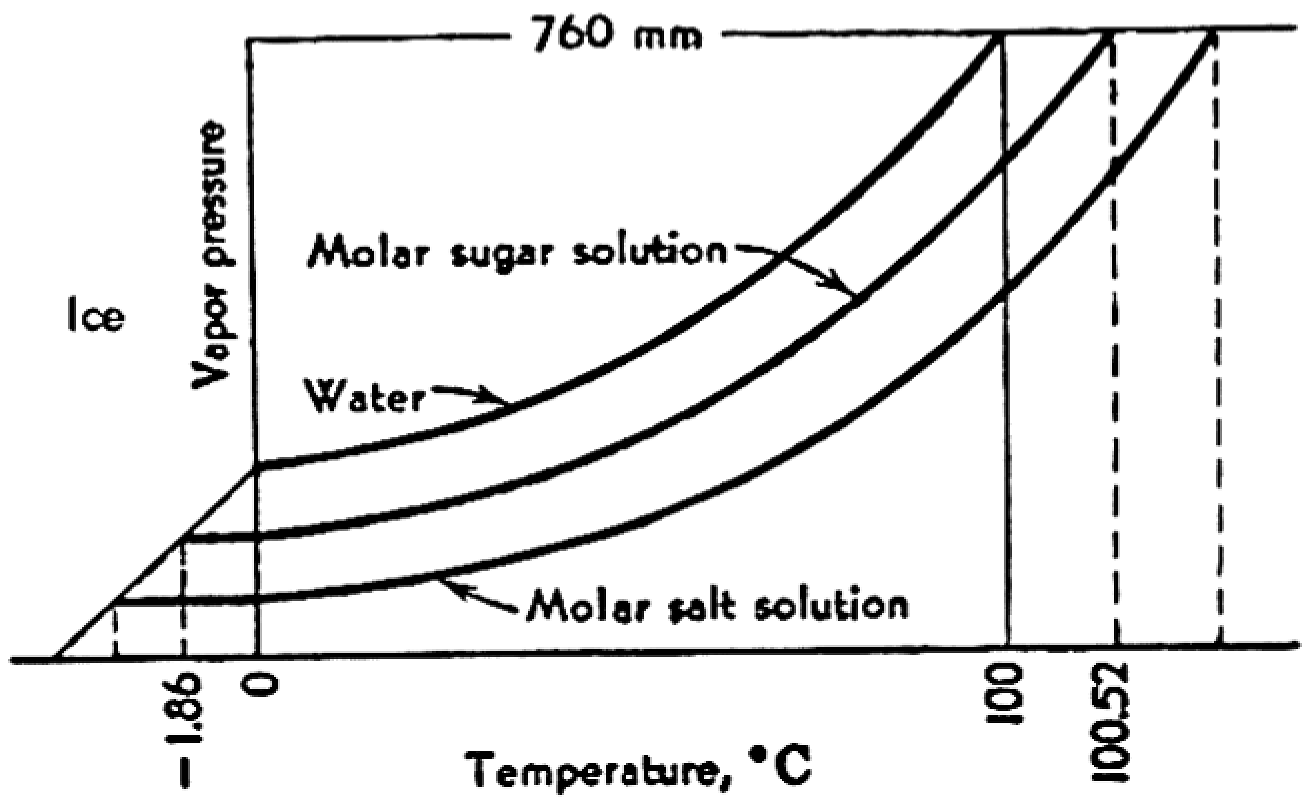


FIG. 47. The vapor pressure of an electrolyte solution lies below that of water and below that of a non-electrolyte solution of the same concentration. Consequently the freezing point is lower and the boiling point higher.

more particles of sodium chloride were operating (to lower the vapor pressure) than we actually put into solution.

If we now look at Fig. 47 to the left of the 0°C line we see that the molar sodium chloride solution curve cuts the vapor pressure curve of ice still farther below 0°C than the sugar solution curve. Consequently, the freezing point of the solution will be still lower than −1.86°C. Since the freezing point depression, as we have agreed, varies directly with the concentration, it looks as if more particles of sodium chloride were operating (to depress the freezing point) than we actually put into solution. Generally we can say that the *freezing point of a solution of an electrolyte is always lower than that of a non-electrolyte of comparable concentration,* that is, abnormally low according to Raoult's law. This becomes all the more striking when we realize that 58.5 grams of common salt can be more effective in melting ice than 342 grams of cane sugar, since these are the gram molecular weights of the compounds concerned.

A parallel occurrence is found in that part of Fig. 47 to the right of the 100° line. Here the molar salt solution curve cuts the atmospheric pressure line (760 mm) even farther on than the molar sugar solution curve. This means that, in general, *the boiling point of an aqueous solution of an electrolyte is always higher than that of a non-electrolyte of comparable concentration*, that is, abnormally high from the point of view of Raoult's law. Again it appears as if more sodium chloride particles were operating (to elevate the boiling point of water) than were actually put into solution.

Summing up the foregoing facts, we are justified in stating that solutions of electrolytes show abnormal values for vapor pressure, freezing point depression and boiling point elevation. It should be noted that we have not used a gas or liquid as solute in this example. A gas will leave the solution on heating, and the vapor pressure of the solution at any temperature is not that of the water alone. A liquid can be used just so long as it has a negligible vapor pressure at 100°C, but not otherwise.

The osmotic pressure of a sugar solution containing the gram molecular weight in 22.4 liters of water at 0°C is 1 atmosphere. The corresponding solution of sodium chloride shows a much higher osmotic pressure—about 2 atmospheres. In this property also the effect of the presence of an electrolyte is abnormal. What is true for sodium chloride is equally true for other electrolytes.

The explanation of these abnormalities must account for the apparently greater number of particles operating than can be listed under the name of whole molecules. This explanation was provided by Arrhenius (in 1887) as follows: *When an acid, a base or a salt is dissolved in water, its molecules break up* [some or all of them] *into simpler particles called ions; these ions are electrically charged.* The proof of this explanation is given by electrical conduction. It is easy to test this by means of the apparatus shown in Fig. 48; here the pair of platinum plates (called *electrodes*) may be dipped into a solution. If the solution conducts the current, then a current will flow from the dry cells and illuminate the lamp; if no glow is noticed in the lamp, this lack of conduction of electricity indicates a non-conductor or non-electrolyte. This form of apparatus can be used to test other

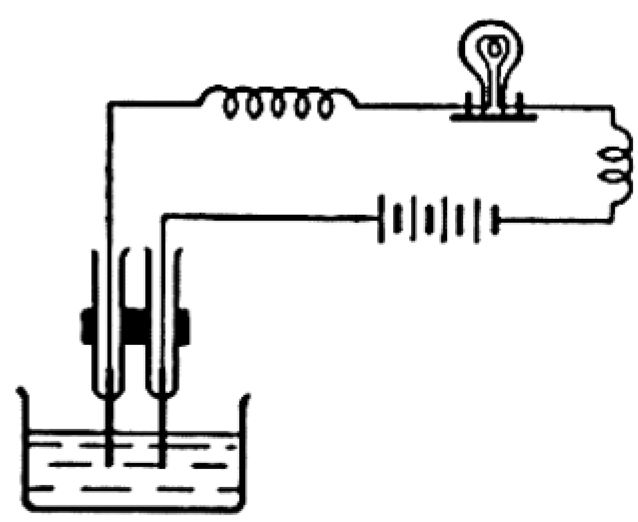


FIG. 48. A simple apparatus for testing the conduction of electricity by different bodies.

substances, such as a solid, by touching both electrodes at the same time to the lump or bar. The following tabulation shows the results of such testing, + indicating conduction and − indicating none.

TABLE 7

Roll sulfur −	Mercury +
Pure water −	Graphite +
Dry HCl (gas) −	Aqueous HCl +
Dry NaOH (solid) −	Aqueous NaOH +
NaCl (solid) −	Aqueous NaCl +
Pure acetic acid −	Aqueous acetic acid +
Crystalline copper chloride −	Aqueous copper chloride +
Crystalline silver nitrate −	Aqueous silver nitrate +

Continuation of this test with, say, copper chloride will show copper being deposited on one of the electrodes (the one connected with the negative pole of the battery of cells); contrariwise, chlorine will be liberated from the other electrode (the positive pole of the battery). If we regard the negative electrode (called the *cathode*) as a plate covered with a negative charge of electricity, the attraction to it of copper particles means that these copper particles are positively charged when in solution—the Arrhenius copper ion. In a parallel sense, the attraction of chlorine ions to the positively charged electrode (called the *anode*) means that these ions are negatively charged—the Arrhenius chlorine ion.

179 Degree of Ionization

If two electrodes (as in Fig. 48) are put into pure acetic acid no appreciable current will be conducted. But on the addition of a quantity of water, some current will be registered by the lamp; on adding more, still more current is observable. This increase continues until no greater conduction is apparent. This point of dilution, called commonly *infinite dilution*, represents the condition where no more ions are appearing to carry current. At any dilution from zero up to infinite, only some of the molecules are dissociated to carry the current; this was called *degree of ionization* by Arrhenius.

Arrhenius' ionization theory proposed that all electrolytes are not dissociated to the same extent. Some, such as hydrochloric acid, nitric acid and sodium chloride, are nearly completely ionized; others like acetic acid and ammonium hydroxide are

slightly ionized; still others have intermediate values. The degree of ionization of a particular substance has been measured by various methods, and all give fairly congruent results. These methods involve a comparison between the actual freezing point depression and the calculated depression, and similar comparisons of boiling point and of osmotic pressure. A simpler method is based on electrical conduction. If we assume that in an aqueous solution of finite (not infinite) dilution an equilibrium exists between the conducting and non-conducting portions of the solute, that is,

$$\underset{\text{Non-conducting}}{NaCl} \rightleftharpoons \underbrace{Na^+ \quad + \quad Cl^-}_{\text{Ions, conducting}} \tag{79}$$

the measurement of conductivity at that dilution will be a fraction of the conductivity at infinite dilution. The degree of ionization is equal to $\dfrac{\text{Conductivity at finite dilution}}{\text{Conductivity at infinite dilution}}$. The result of this observation is a fraction, which may also be expressed as percentage, showing what proportion of the solute is actually ions carrying the current.

A substance which shows a high percentage of ions in solution is a *strong electrolyte;* one showing a small percentage, a *weak electrolyte;* one in between these two extremes is *medium.* Table 8

TABLE 8

APPARENT PERCENTAGE OF IONIZATION

0–2 per cent (*Weak*)		*20–90 per cent* (*Medium*)		*90–100 per cent* (*Strong*)	
HAc	1.34	H_2SO_4	61	HCl	92
H_2CO_3	0.17			HNO_3	92
H_2S	0.07	$Ba(OH)_2$	81		
H_3BO_3	0.01				
				NaOH	91
NH_4OH	1.3	$ZnSO_4$	41		
		$MgCl_2$	73		
Water	0.0000001	NaCl	85		
		KCl	86		

shows this apparent degree of ionization for solutions made up to contain the quantity of solute equivalent to 1 gram of hydrogen per liter at 18°C.

180 The Debye-Huckel Theory of Ionization

The previous study of solutions of electrolytes has been based on the valuable contribution to science first made by Arrhenius. In brief, his theory was that electrolytes may exist in solution as an equilibrium between non-conducting or un-ionized molecules and freely conducting ions. This theory is satisfactory for dilute solutions of weak electrolytes but does not explain that certain substances may be electrolyzed in the fused state, that is, when

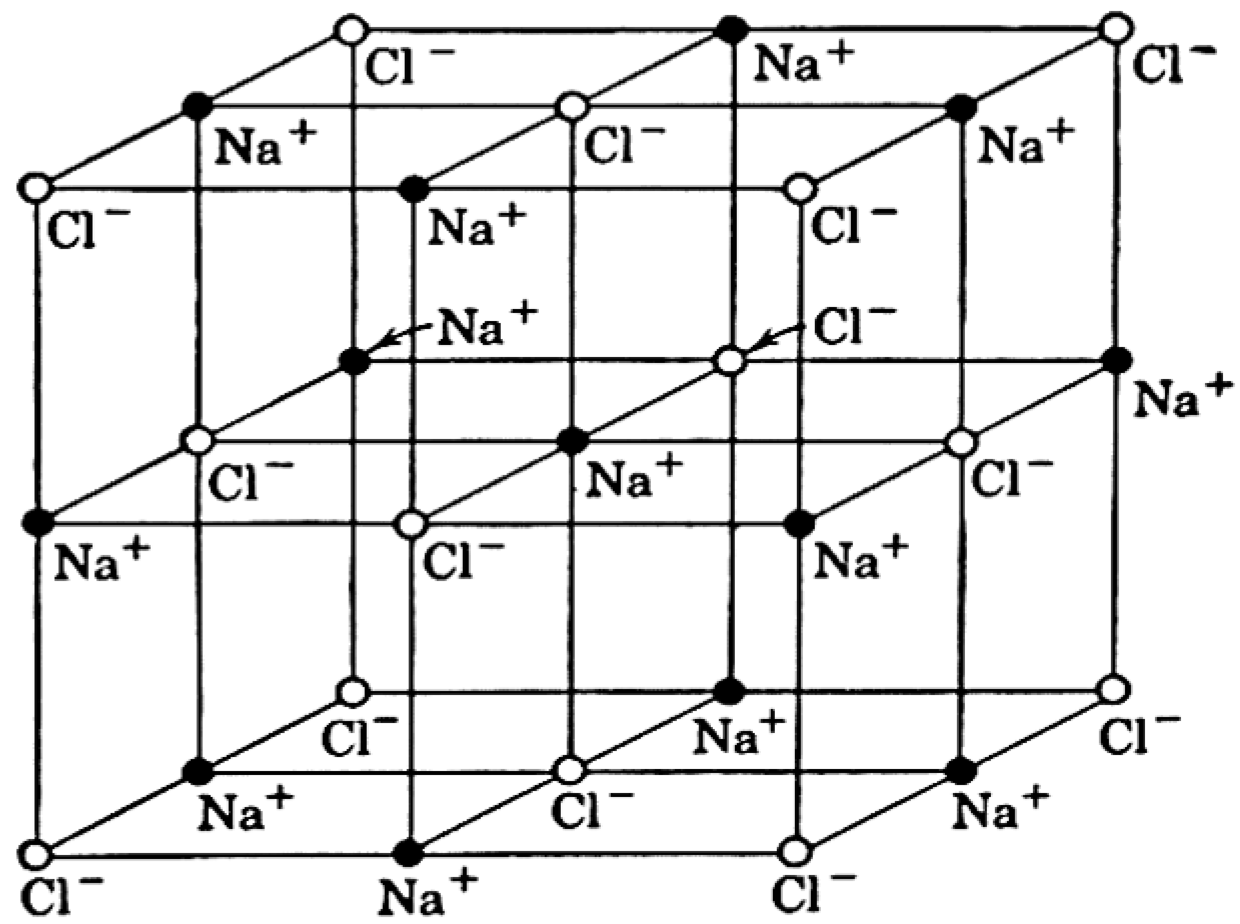


FIG. 49. X-ray pictures of a crystal of sodium chloride show that in any one plane the ions of sodium and of chlorine occur alternately.

melted rather than dissolved in a solvent like water. Magnesium chloride ($MgCl_2$), when free of water and molten, will conduct the electric current; magnesium metal is collected at the cathode, and chlorine is evolved at the anode. Obviously the fused salt must contain ions. Since no solvent is involved it may be suspected that magnesium chloride is ionized even in the solid state.

Another instance is afforded by sodium chloride, which is 85 per cent ionized in 0.1 N solution at 18°C (see Table 8); that is, according to the Arrhenius theory, 15 out of every 100 molecules dissolved in water at the above concentration is not in the form of ions but of molecules. This does not agree with the X-ray picture of crystalline sodium chloride, which shows ions of sodium and ions of chlorine in alternate positions (Fig. 49). The fact to be faced, therefore, is that solid sodium chloride is 100 per cent ionized. It follows therefore that it should be 100 per cent ionized when fused or when dissolved in water in any concentration.

The Debye-Huckel theory (proposed in 1923) considers *strong acids, alkalies and salts to be completely ionized before dissolving in water.* In solution each ion may be surrounded by a cluster of solvent molecules, providing what is called an "ionic atmosphere" (Fig. 50). Any ion so surrounded is not able to act as a "free ion" and move at will; it is a "bound ion." The *free ions* are those which can respond to electrical attraction and can be collected at the cathode and anode, thus producing electrical conductivity. The

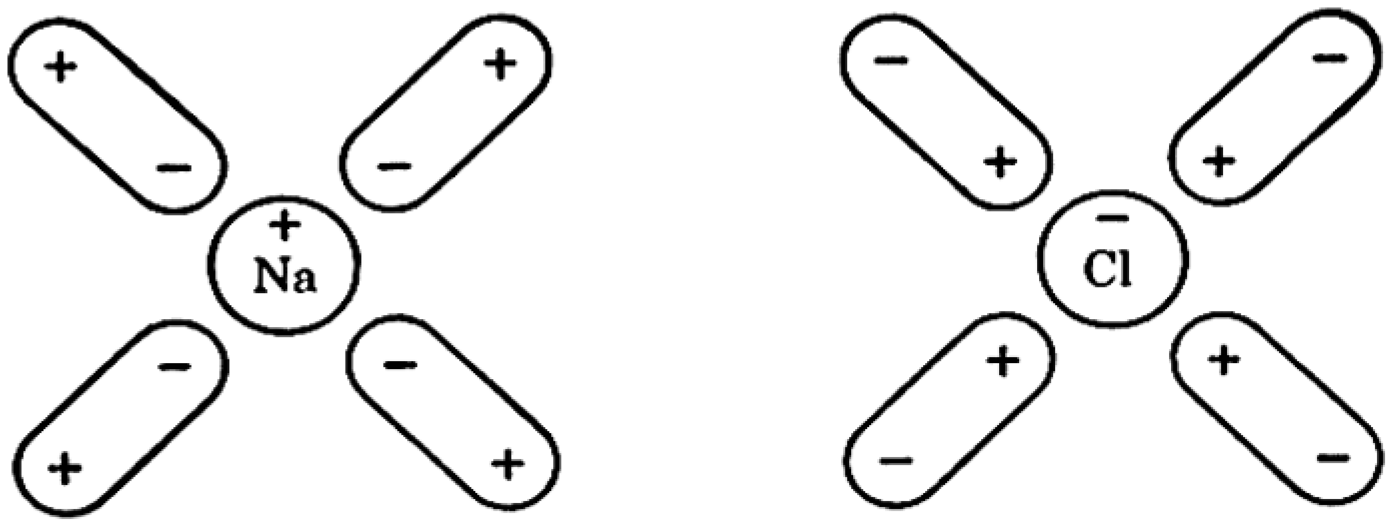


FIG. 50. The ions of sodium and of chlorine may be imagined as surrounded by solvent molecules causing them to be bound and not free to conduct the current; this illustrates ionic atmosphere.

bound ions, unable to conduct the current, correspond to Arrhenius' un-ionized molecules.

An explanation is also afforded of how the ionization of a solution apparently increases with dilution. The more dilute the solution the farther apart the ions are; hence the freer they are to move. Other explanations of discrepancies in the Arrhenius theory are provided by the Debye-Huckel theory. On the main principles, however, there is considerable agreement, such as the charges on the ions, the reversible equilibrium (between bound and free ions) and the apparent degree of ionization.

181 Rate of Ionic Reaction

If, in the above reactions, a dilute aqueous solution of the alkali is added all at once to the acid in similar solution, neutralization will take place immediately. Another such example is adding aqueous barium chloride to aqueous sodium sulfate, when a precipitate of barium sulfate occurs instantaneously. Non-electrolytes usually react slowly—further evidence for the different behavior of electrolytes. Consequently, the molecular equation

$$BaCl_2 + Na_2SO_4 \rightarrow 2NaCl + BaSO_4 \downarrow$$

is incorrect from the point of view of what actually occurs and should therefore be written thus:

$$Ba^{++} + 2Cl^- + 2Na^+ + SO_4^{--} \rightarrow$$
$$2Na^+ + 2Cl^- + BaSO_4 \downarrow \quad (80)$$

The most apparent characteristic of reactions between electrolytes is, therefore, their rapidity, which is so great as to be regarded as instantaneous.

182 Electrolysis and Faraday's Laws

Early in the history of the conduction of electricity by aqueous solutions and long before the nature of ions was understood, Michael Faraday discovered a definite connection between the quantity of electricity used and the amount of substance that could be deposited on an electrode. To measure a quantity of electricity we may use an instrument to record amperes and an instrument to measure time. The practical unit of electricity is the *coulomb*, which is the quantity of electricity that passes a point in a circuit in one second when a current of one ampere is flowing. This is comparable to measuring the amount of water that flows through a pipe for an extended period of time when we know the amount that passes through a water meter each second. Thus if a current of 2 amperes flows through a circuit for 1 hour (3600 seconds), the quantity of current carried by the circuit in that time is

$$2 \times 3600 \text{ coulombs} = 7200 \text{ coulombs}$$

Faraday enunciated two laws, which may be summed up as follows:

(1) *The same quantity of electricity will liberate weights of elements in proportion to their equivalent or combining weights.*

(2) *The quantity of electricity required to liberate one gram equivalent weight of an element is 96,500 coulombs.*

The following experiment illustrates these laws (see also Fig. 51).

Arrange three cells to contain solutions of silver nitrate ($AgNO_3$), copper chloride ($CuCl_2$), and sulfuric acid (H_2SO_4), respectively. Provide each with electrodes of silver, copper and platinum, respectively, and connect them in series with a battery and an ammeter. Weigh the electrodes for the silver nitrate and copper sulfate solutions before the current is turned on and arrange to

collect and measure the volumes of gases produced from the sulfuric acid. Now turn on the current and adjust the battery to keep the current at some one value. Measure the time the current flows. Let us suppose the current flows until just 107.88 grams of silver have deposited on the cathode in the silver nitrate solution. The product of the ammeter reading and the stop-watch reading at this time will show that 96,500 coulombs have passed through each solution. It will be found that the positive silver electrode or anode has lost in weight exactly what the cathode has gained. Similarly, 63.6/2 grams of copper (one equivalent or combining

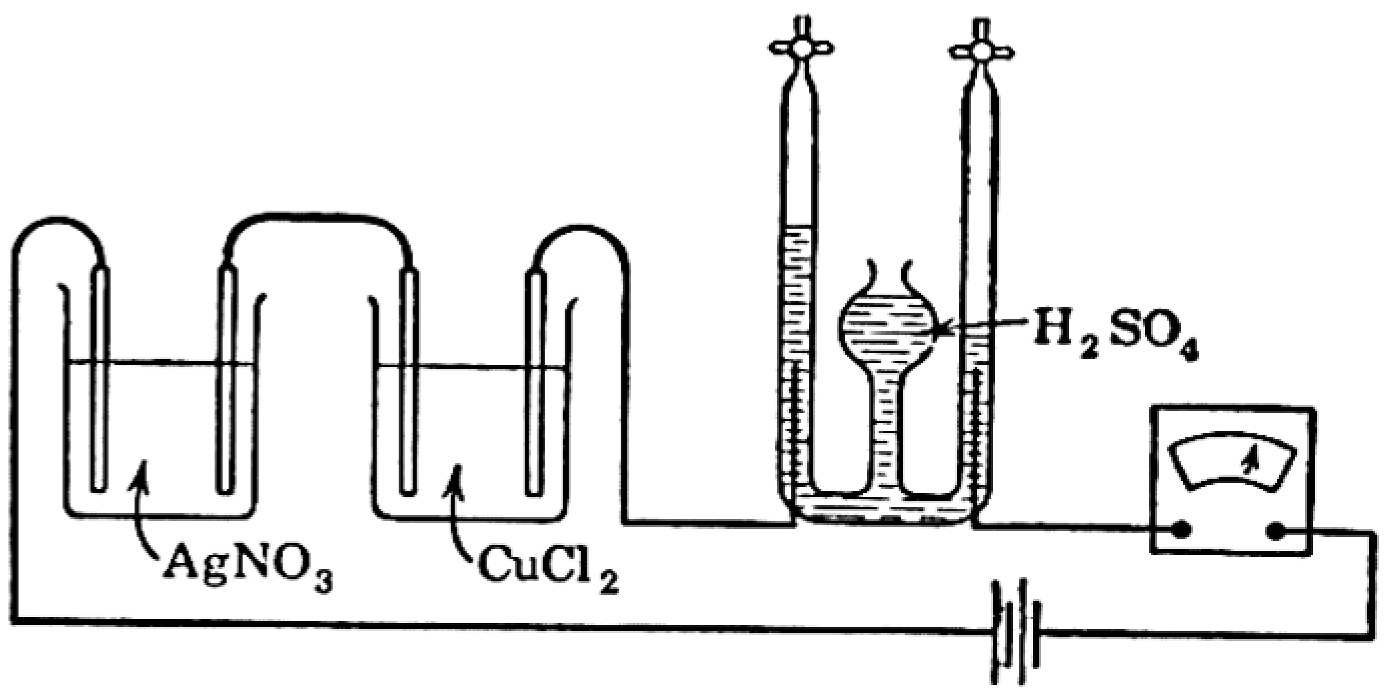


FIG. 51. Illustrating the experiment to show the quantity of electricity required to liberate one gram equivalent weight of an element (Faraday's laws).

weight) has dissolved from the anode in the copper chloride solution, and exactly the same amount has been deposited on the copper cathode; 11.2 liters of hydrogen gas and 5.6 liters of oxygen gas measured at standard temperature and pressure will be collected at the cathode and anode respectively in the sulfuric acid solution. In short, the passage of 96,500 coulombs of electricity has deposited or dissolved exactly one equivalent weight of an element at each electrode.

It will be remembered that the equivalent weight of an element is found by dividing the atomic weight by the valence. Silver is monovalent; hence the equivalent weight is the same as the atomic weight. The valence of copper (as in $CuCl_2$), however, is 2, so that its equivalent weight is one half the atomic weight. Faraday found by experiment the amount of each element liberated by one coulomb of electricity; this he called the *electrochemical equivalent.* Our knowledge now enables us to calculate this value by dividing the gram equivalent weight of the element by 96,500. The same

end is achieved by using the formula $\frac{\text{Gram atomic weight}}{\text{Valence} \times 96{,}500}$. This value for silver is $\frac{107.88 \text{ grams}}{1 \times 96{,}500} = 0.001118$ gram.

183 Neutralization

When 40 grams of sodium hydroxide (gram molecular weight) react with 36.5 grams of hydrogen chloride (gram molecular weight) in aqueous solution, a definite amount of heat is liberated. The molecular manner of expressing this reaction is

$$NaOH + HCl \rightarrow NaCl + H_2O + 13{,}700 \text{ calories} \quad (81)$$

But our previous experiments have shown that aqueous NaOH, HCl and NaCl are all electrical conductors but that water is not to any great degree. To be consistent, we must therefore represent these reagents in the ionic condition: $Na^+ + OH^- + H^+ + Cl^-$. The possible recombinations amongst these ions will result in NaOH, NaCl, HCl and H_2O, but not in NaH and OHCl because of their similar charges. Water is the only one of the four compounds in equation 81 which is un-ionized. Hence the following is the correct representation of the reaction:

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow$$
$$Na^+ + Cl^- + H_2O + 13{,}700 \text{ calories} \quad (82)$$

This is *neutralization* since the OH^- ions of the alkali and the H^+ ions of the acids, which have their separate effects in changing the color of an indicator, no longer exist free but as H_2O molecules.

In similar reactions between KOH and HCl, NaOH and HNO_3, etc., a constant quantity of heat is evolved, 13,700 calories. This suggests (1) that in a neutralization only water molecules are formed and that by the combination of H^+ and OH^-; (2) that the heat produced for this liberation of H_2O is the same; and (3) that the union of 1 gram of H^+ ions and 17 grams of OH^- ions liberates a constant quantity of heat, known as the *heat of neutralization.*

184 Hydrolysis of Salts

The word *hydrolysis,* when divided into *hydro* and *lysis,* means "water" and "loosening." That is, a "loosening" takes place and water is responsible for it (compare electrolysis). This is a very common reaction with wide application, as we shall see later.

In this particular study it must be regarded as the reverse of neutralization. A type reaction of neutralization is

$$\underset{\text{Acid}}{HX} + \underset{\text{Base}}{BOH} \rightarrow \underset{\text{Salt}}{BX} + \underset{\text{Water}}{H_2O}$$

If BX, however, is a *certain kind* of salt, this action can be reversed. This reversal is possible by adding an excess of water, and, although we commonly look on water as being un-ionized, it is sufficiently ionized to cause a reaction with this kind of salt. The reversal of the above equation becomes

$$\underset{\text{Salt}}{BX} + \underset{\text{Water}}{HOH} \rightarrow \underset{\text{Acid}}{HX} + \underset{\text{Base}}{BOH}$$

Salts generally may be divided into four classes: (1) salts of strong bases and strong acids; (2) salts of strong bases and weak acids; (3) salts of weak bases and strong acids; (4) salts of weak bases and weak acids.

The first class of salts will not hydrolyze. The remaining classes of salts will hydrolyze.

Sodium acetate, of the second class, is a salt made from the strong base NaOH and the weak acid CH_3COOH; it hydrolyzes according to the equation

$$H_2O + Na^+ + CH_3COO^- \rightleftharpoons Na^+ + OH^- + CH_3COOH \quad (83)$$

The solution is basic.

In the third class ferric chloride is a salt of the very weak and almost insoluble ferric hydroxide and HCl; it hydrolyzes thus:

$$3H_2O + Fe^{+++} + 3Cl^- \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^- \quad (84)$$

The addition of sufficient water will cause the ferric hydroxide to precipitate; the solution is acidic.

In class four lead acetate in dilute solution hydrolyzes rapidly to produce lead hydroxide and acetic acid:

$$2H_2O + (CH_3COO)_2Pb \rightleftharpoons Pb(OH)_2 \downarrow + 2H^+ + 2CH_3COO^- \quad (85)$$

The resulting solution is acidic.

185 Hydration

Very many solids which are soluble in water are known to possess a crystalline form, that is, they have faces and angles characteristic of one or the other of the crystal systems. Sodium carbonate is

found to crystallize from solution in water when the water is slowly evaporated off; and these crystals, on standing in a dry place, become powder and lose weight. This loss in weight is caused by loss of water by evaporation. In the crystalline state, then, sodium carbonate contains water of hydration or, as it is more commonly called, *water of crystallization.* In writing the formula for these crystals the water molecules are kept separate, since they are so easily lost—sodium carbonate, $Na_2CO_3 \cdot 10H_2O$. The spontaneous loss of water of crystallization is called *efflorescence.* But not all crystalline bodies contain water of crystallization, for example, common salt, sugar, diamond and quartz, for water is not essential to crystalline form.

The behavior of calcium chloride is the reverse of efflorescence. When this substance is dry and is exposed to a moist atmosphere, it absorbs water very readily from the atmosphere—so much so that it will dissolve in it to form a concentrated solution of calcium chloride in water. This phenomenon is called *deliquescence.* Sodium and potassium hydroxides, as well as some zinc salts, behave the same way. Because of this property, calcium chloride is much used for keeping gravel roads free from dust, since it becomes moist and absorbs the dust. Actually, efflorescence and deliquescence are different aspects of the same property—the ability of some substances to be hydrated or to hold in their molecules water of hydration. Nor is this property confined to solids since sulfuric acid, a liquid, shows it.

Whether a solid is deliquescent or efflorescent depends largely on the humidity of the atmosphere to which it is exposed. In other words, efflorescence and deliquescence are opposite phases of the same property—the ability to absorb water.

186 Review of Definitions

Electrolytes are substances which in aqueous solution will conduct the electric current. Non-electrolytes do not do so.

Degree of ionization refers to the extent to which ions in solution are free to carry the current.

Infinite dilution is that dilution (usually very large) at which all ions present are free and conducting the current.

A strong electrolyte is one which shows a high electrical conductivity in a solution of fixed concentration; a weak electrolyte is one which shows a low electrical conductivity under similar circumstances.

A coulomb is the quantity of electricity which passes a point in an electrical circuit in one second, when a current of one ampere is flowing.

Neutralization is the reaction of a base with an acid to produce water and a salt.

Hydrolysis is the reaction of a salt with water to produce an acid and a base; it is thus the reverse of neutralization.

187 Summary

The rules governing vapor pressure, freezing point, boiling point and osmotic pressure are known to hold for all substances in aqueous solution just so long as these solutions do not conduct the electric current. Such substances are called non-electrolytes.

Electrolytes are those substances which, particularly in aqueous solution, conduct the electric current. They are divided into three classes: acids, bases (really alkalies) and salts.

Solutions of electrolytes show abnormally low vapor pressures and freezing points and abnormally high boiling points and osmotic pressures when compared to non-electrolytes. Since the degree to which these phenomena are abnormal depends upon the number of particles in solution, it must follow that electrolytes must give rise to more particles than non-electrolytes.

These abnormalities and the theory of dissociation of electrolytes receive their confirmation in the electrical conduction of aqueous solutions. The single molecule of the non-electrolyte is replaced by the ions (2 at least) of the electrolyte. Ions are of two kinds, one carrying one or more positive charges and the other carrying one or more negative charges, depending on the valence. Ions collected at the cathode are called cations and are positively charged, whereas those collected at the anode are called anions and are negatively charged.

At different dilutions electrolytes conduct to different degrees, explained by the fact that it is only the free ions which can carry the current; hence the term *degree of ionization.* Whereas the Arrhenius theory considered non-conducting ions to be still in the molecular form, modern theory supposes all solute electrolytes to be present as ions—some "bound," some "free."

Electrolytes are called weak or strong, depending on their degree of ionization at the same dilution.

Ionic reactions are practically instantaneous; the union of ions is caused by the electrical attraction of ions of unlike sign.

Faraday's laws of electrolysis are now intelligible; 96,500 coulombs will liberate the gram equivalent weight of an ion.

Neutralization is the reaction between hydrogen and hydroxyl ions to produce water which is relatively un-ionized. The reverse of neutralization is hydrolysis, which occurs in all salts which are not formed from both strong acids and strong bases.

Questions

1. Show how the freezing point, boiling point and osmotic pressure of solutions differ when (*a*) a non-electrolyte and (*b*) an electrolyte are dissolved in water.

2. How does electrolysis help to explain the situation in the previous question?
3. Write equations showing the ionization of the following: KCl, KNO_3, $CaCl_2$, $AlCl_3$, H_2SO_4, $Ca(OH)_2$.
4. State in one sentence why reactions between electrolytes should be more rapid than those between non-electrolytes.
5. Define molecule and ion in such a way as to show the difference between them.
6. State concisely what you consider to be the essentials of neutralization.
7. What are the Faraday laws respecting electrodeposition?
8. What significance do you attach to the value 96,500 coulombs?
9. What do you understand by the terms (*a*) degree of ionization, (*b*) infinite dilution?
10. Name the kinds of salts which can show hydrolysis.
11. State concisely why the Debye-Huckel theory was enunciated.
12. Explain briefly the terms "bound" and "free" when applied to ions.
13. (*a*) If a current of 0.3 ampere flows for 27 minutes how many coulombs are carried? (*b*) If the atomic weight of gold is 197 and its valence 3, how much gold should be deposited by the current in the previous question?

15

Colloidal Solutions

188 True Solutions

When a solid or a liquid dissolves in water and distributes itself uniformly throughout the body of the water it does so automatically, a little heat being given off or absorbed—called *heat of solution*. The resulting solution is called a true solution if it obeys the laws relating to vapor pressure, boiling point, freezing point and osmosis whether it contains a non-electrolyte or electrolyte. Furthermore it looks clear to the eye when strongly illuminated and observed under a microscope, even if colored.

189 Colloidal Solutions

A liquid or a solid which does not dissolve in water automatically, for example, gasoline or chalk, might conceivably be induced to do so if subdivided into molecules. This division would involve considerable mechanical agitation of the liquid with the solvent, and extraordinarily fine grinding of the solid. But many liquids and solids exist in solution in the associated condition, so that it might not be necessary to subdivide an insoluble substance as far as individual molecules. Small molecular aggregations might suffice to stand up in the solvent instead of precipitating to the bottom or floating on top of the solvent. Actually we can do just that, for example, with the colloid mill, which is specially designed to reduce large solid aggregates to smaller ones well beyond the capacity of the ordinary grinding machines.

190 Examples of Colloidal Solutions

(1) If about 20 ml of water and 5 ml of gasoline are poured into a stoppered glass cylinder, two layers will appear, the lighter gasoline floating on the surface of the heavier water. After violent

shaking, these volumes break up into smaller portions, so that on standing there first appears a milky mixture; but this uniformity, at first apparent, rapidly disappears, and in a very short time there are again two distinct layers in the cylinder. Now if a few drops of concentrated soap solution are added to the liquids with shaking, a milky mixture is produced whose uniformity will remain for a longer period. Addition of sufficient soap solution produces what is commonly known as an emulsion of oil and water. This emulsion differs in appearance from the separate gasoline and water layers in being distinctly opalescent (see Fig. 52).

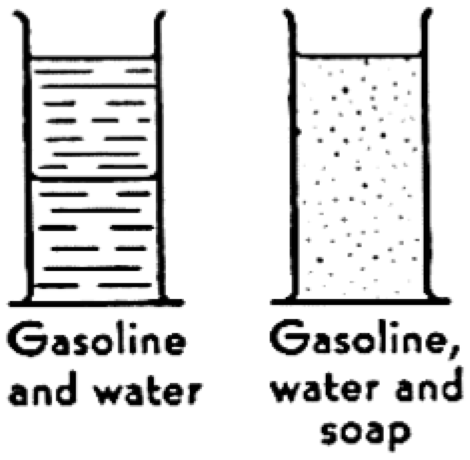


FIG. 52. Soap is an emulsifying agent.

(2) Again, if hydrogen sulfide gas is passed into a concentrated solution of arsenious chloride, a thick yellow precipitate of arsenious sulfide results:

$$2AsCl_3 + 3H_2S \rightarrow As_2S_3 \downarrow + 6HCl \qquad (86)$$

Here the tiny molecules of the sulfide coagulate to form aggregations which are too large to remain suspended and so are thrown down to the bottom of the container, leaving a clear liquid above. But if a dilute aqueous solution of hydrogen sulfide is slowly added, with stirring, to a dilute solution of arsenious chloride, the same chemical reaction takes place except—and this is important—that no precipitate results, though the solution becomes quite definitely opalescent.

(3) A small amount of solid glue added to water will gradually dissolve to form a gummy solution which may appear clear to the naked eye. But if a small, intense beam of light is passed through such a solution, the path of the beam will be quite visible, like sunlight streaming into a smoky room.

(4) Metallic gold is insoluble in water. If, however, two pieces of gold wire are connected to a source of electricity, brought together under water to complete the circuit and then withdrawn a short distance so that an arc forms under water, a cloud will be seen to form around the arc and gradually diffuse throughout the whole volume of liquid. This cloudiness, which is usually colored, is caused by the presence of very fine particles of gold. too large to be invisible and too small to precipitate.

All the examples above have one thing in common, that they render visible a beam of light passed through them. This is not true of the solution of electrolytes and non-electrolytes previously studied. This optical property is known as the Tyndall effect.

We have now three types of aqueous solution: (1) non-electrolytic; (2) electrolytic; (3) colloidal. One and two are frequently considered together under the heading of true solutions, as colloidal solutions were originally thought to be quite different from them. It must be realized, however, that the difference is in degree, not in kind, as will appear in the following paragraphs.

191 The Language of Colloids

Though the word *colloid* is derived from a Greek word meaning glue, not all colloids are of the gluey kind. Indeed it may be said that any pair of substances can give rise to a colloidal solution. Aqueous solutions may contain solute particles as small as the hydrogen ion and so large that any slight increase in size causes them to precipitate out (or, in the case of a liquid or gaseous solute, to rise to the surface). Within that size range come all the three types mentioned.

Where the size of the particles is such as to show the Tyndall effect, special terms are employed. Below is a comparative table showing some of these terms:

TABLE 9

COMPARATIVE TERMS

For True Solutions	*For Colloidal Solutions*
Solvent	Dispersion medium
Solute	Dispersed phase
Solution	(Liquid in liquid) Emulsoid
Solution	(Solid in liquid) Suspensoid
	(and generally) Dispersoid, or colloidal solution

Any substance which can be dispersed throughout a medium without producing a true solution becomes, therefore, a colloid.

As a rule a liquid may be dispersed in a liquid (*emulsoid*), then separated, dispersed again and so on indefinitely. Such a colloid is reversible or *lyophyllic* (liking solution). Glue and gelatin are

in the same class, although they are *suspensoids.* On the other hand, those colloids which, when once precipitated out of solution cannot be put back again directly, are known as irreversible or *lyophobic* (hating solution); they are commonly insoluble solids, such as gold, silver, arsenious sulfide, ferric hydroxide.

192 Methods of Preparing Colloidal Solutions

These methods are of two general types, (1) *dispersion* and (2) *condensation.* There are these subdivisions of dispersion. (1) *Electrical disintegration* occurs when an arc is formed under water between metal wires (as previously explained). (2) In *peptization* a large molecular aggregation is broken up by treatment with an alkaline solution; it is somewhat similar to digestion. (3) *Mechanical disintegration* occurs in grinding. (4) *Emulsification* took place in our oil-water-soap experiment previously mentioned. Examples of condensation methods were given in the ferric hydroxide and arsenious sulfide experiments. They are somewhat similar to polymerization, to be described under organic chemistry.

193 Some Properties of Colloidal Solutions

(1) *The Tyndall effect.* When a powerful beam of light is passed through a colloidal solution, an observer who views the solution at right angles to the path of the light will observe an opalescence due to the scattering of light by the clusters of molecules.

(2) *Electrical conductivity.* Some colloidal particles are electrically charged, and those mainly in suspensoids. When charged and subjected to the passage of a direct electric current, however, the whole particle goes in one direction only. This is called *cataphoresis* and indicates not two oppositely charged particles like ions, but particles all with the same kind of charge. The presence of a charge of any kind, as well as its sign, will depend mainly on the method of preparing the colloidal solution.

(3) *The vapor pressure,* freezing points, boiling points and osmotic pressures of colloidal solutions are very nearly the same as those of the solvent or dispersion medium. They thus differ from non-electrolytic solutions and differ very greatly from the electrolytic or ionic.

(4) *The Brownian movement.* When viewed in the ultramicroscope, a colloidal suspension shows numerous spots of light, which are darting hither and thither in a zigzag manner (Fig. 26). This

is known as the Brownian movement. These motions would appear to be caused by bombardment of the colloidal particles by water molecules and may well represent the motion of particles in any non-viscous medium.[1]

(5) *Permanence of the colloidal state.* When appropriately prepared, colloidal solutions will stand up indefinitely in a closed system. But the preparation of the gasoline-water solution involves the use of a small amount of soap, itself a colloid, and known here as a *protective colloid.* Gelatin and many other substances act similarly. The colloidal condition may be destroyed in a variety of ways, of which the following are illustrative. Egg white or egg albumin may be coagulated by boiling, that is, the relatively large colloidal aggregations of fluid egg material form much larger aggregations under the influence of heat and so set to an insoluble mass occluding all the water in which the albumin was formerly dispersed. If to colloidal ferric hydroxide, whose particles are positively charged when prepared as stated previously, there is added an ionogen such as sodium sulfate, the negatively charged sulfate ions tend to neutralize the positive charges on the ferric hydroxide, causing it to coagulate and eventually precipitate. This precipitation occurs on a large scale where rivers, containing suspended and electrically charged mud particles, come in contact with the ocean with its high content of sodium chloride and other charged ions, forming the well-known deltas at the river mouth. Again, the protective colloid in cow's milk is susceptible to heat treatment, so that, on heating, the cream (fat and protein largely) separates out. Of course, the evaporation of the dispersion medium (water in the case of household glue) will cause precipitation of the suspended colloid since there is insufficient medium left for its dispersion.

(6) *Viscosity and surface tension.* These two properties may show considerable variation, as exemplified by milk and egg white. A soap solution always shows a remarkable change in surface tension from that of water, and aids in the collection of dirt particles during washing. Likewise surface tension enters into the strange behavior of oils in water, of such importance in the flotation of ores. That the surface tension of a colloidal solution may

[1] An ultramicroscope is a microscope placed at right angles to a cell containing the solution to be viewed, this cell being illuminated by a very powerful but thin pencil of light.

change greatly for small concentration changes is illustrated by the setting of gelatin. Whereas a dilute solution of 2 or 3 per cent gelatin is fluid, a 5 per cent solution will, on standing, set to a semi-solid mass of high viscosity and surface tension. Because of this phenomenon, freely flowing colloidal solutions are commonly called *sols*, whereas one which has "set" in the above sense is referred to as *gel*.

(7) *Surface adsorption.* When we speak of absorption, we think of a porous body being filled with some other material, for example, a sponge absorbing water. Adsorption is the retention of some body on the surface of another. Obviously, the larger the surface area of the adsorbing material the greater the amount of other material which can be adsorbed. Now colloidal particles have a very great surface and so may be used to adsorb large quantities of suspended particles. Aluminum hydroxide, a somewhat gelatinous mass, can be used to clarify other colloidal solutions; other examples are the clarification of sugar by bone ash, the bleaching of oils by fine clays and the fixing of colors in textiles.

(8) *Particle size.* The largest particles reflect light, as shown by the Tyndall effect. The ordinary microscope can detect particles 10 millimicrons in diameter (1 $m\mu$ = one-millionth of a millimeter). Particles one-twentieth of this diameter have been detected; they are relatively large. A diameter of 1 $\mu\mu$ is regarded as the upper limit of size for molecules; the hydrogen molecule is 0.1 $\mu\mu$. A micromicron ($\mu\mu$) = one billionth of a millimeter.

194 The Three Kinds of Aqueous Solutions

Table 10 compares the properties of the three kinds of aqueous solutions. In arbitrarily speaking of three kinds of solutions we do so in order to emphasize the differences that can exist among solutions. It can readily be shown by osmosis that a solute in a solvent behaves like a gas particle enclosed in a container. Perrin, a French physical chemist, was able to demonstrate that the movement of colloidal particles is identical in kind with that of gas molecules, although they might be many thousand times heavier. Actually colloidal particles may be said to exist in a range of magnitude between a large single molecule and a large aggregation of such molecules almost large enough to precipitate.

TABLE 10

PROPERTIES OF AQUEOUS SOLUTIONS

Properties	*True Solutions* Non-electrolytic	*True Solutions* Electrolytic	*Colloidal Solutions*
Electrical	None	Normal conduction + and −	Cataphoresis + or −
Freezing point	Normal	Abnormally large	Abnormally low
Boiling point	Normal	Abnormally large	Abnormally low
Osmotic pressure	Normal	Abnormally large	Abnormally low
Particle size	Molecular	Ionic (submolecular)	Macromolecular
Viscosity	Varies with concentration	Varies with concentration	Varies within wide limits—sols and gels
Surface tension	Varies with concentration	Varies with concentration	Varies within wide limits—sols and gels
Light effect	Any color due to molecules	Any color due to one or more ions	Tyndall effect, and color due to particle size Shows Brownian movement

195 Dialysis

A simple experiment may be performed easily to illustrate how body fluids move through cell walls in a selective manner. If a cuplike sack of parchment paper, containing a solution of common salt and some colloidal matter (for example, egg white), is suspended in a vessel of running water, the ions of the salt will pass outwards into the water, leaving the colloid behind. Thus the selective action of the membrane permits the free passage of the small inorganic ions, while holding back the large colloidal aggregations. This selective separation, known as *dialysis*, is now largely employed for the purification of colloids (Fig. 53).

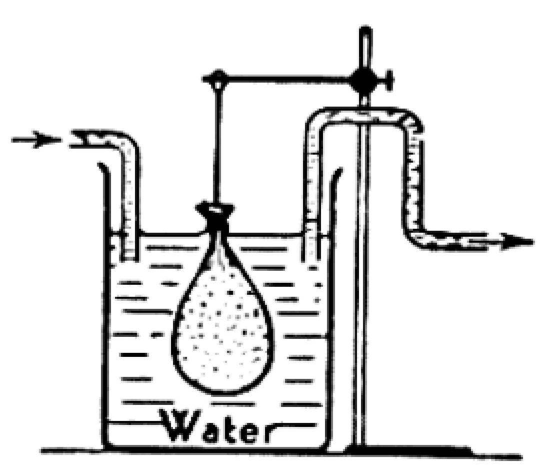


FIG. 53. Dialysis helps to purify colloidal suspensions.

196 Some Applications of Colloid Chemistry

Solidified alcohol is an alcoholic soap gel; it may be prepared by pouring 10 ml of a saturated solution of calcium acetate into

90 ml of 95 per cent alcohol. The two liquids should be contained in small beakers, and poured quickly back and forth until the gel forms. Pieces of the gel may be ignited.

Silica gel has become of great importance for absorbing water vapor and some gases; it is a hydrated form of silica (SiO_2) and a hard glasslike material. It may be made by treating aqueous sodium silicate (water glass) of the correct concentration with hydrochloric acid. It is broken into pieces, washed and dried and is then ready for use.

The cleansing power of soap is due to its forming a colloidal suspension in water. The large surface produced emulsifies the grease and oil and absorbs the dirt.

Tanning occurs when the colloidal particles of tannin attack the colloidal particles in the animal hide, causing the deposition of large, neutral colloidal masses which constitute leather.

The Cottrell process utilizes the fact that fine dust particles may be electrically charged colloidal dispersions. If an electrical conductor in the gaseous flow of a chimney stack gives a charge to particles passing it, these particles may be attracted to a plate of opposite charge and then deposited. This process is useful not merely for eliminating the smoke and dust from chimneys but also for precipitating large quantities of ore-bearing dust from smelters.

The latex of rubber consists of colloidal particles negatively charged. These particles may be precipitated on a rubber-plated anode in much the same manner as electroplating is carried on.

The above are a few of the many applications of colloid chemistry to industry.

197 Summary

Solutions can now be classified as has not been possible previously. Classification is now chiefly a matter of the particle size and whether a particle of solute carries an electrical charge.

Solutions are divided most conveniently into true and colloidal. True solutions obey the laws of solubility and, if non-electrolytic, the rules of freezing point, boiling point and osmosis. If electrolytic, the same regularity is observable but at a higher level of practical values. Colloidal solutions tend to ignore such relationships and to display others.

Though other types are possible and known, the important colloidal solutions are those of liquid-in-liquid and solid-in-liquid, known as emulsoids and suspensoids, respectively.

Colloidal solutions are noted for their interference with the passage of light—the Tyndall effect.

When electrically charged, colloidal particles carry only one sign—hence travel to one electrode only (cataphoresis).

If unstable, colloidal solutions may be stabilized by the addition of another colloid; in consequence, it may be destabilized by elimination of the protection afforded by this other colloid.

If electrically charged, colloidal particles may be precipitated by the addition of an ion (from a true solution) of opposite sign.

Colloidal solutions may be made so as to show the Brownian movement, a zigzag motion illustrating the rapid movement of particles as well as their collision with, and reflection from, other particles.

One property of colloidal particles is the adsorption that can take place on their surface; this is of great industrial importance.

Colloidal particles range in size from the large molecule of a true solution up to the large aggregation just about to precipitate out of solution; this is a considerable range of magnitude.

Questions

1. What classes of aqueous solutions have you studied?
2. How are colloidal solutions related to those which you have previously studied?
3. What two general types of colloidal solutions are there? How may each be prepared?
4. How may the physical properties of a colloidal solution differ from those of, say, cane sugar and sodium chloride?
5. Explain Tyndall effect, cataphoresis, Brownian movement and dialysis.
6. Compare osmosis with dialysis.
7. Name some industrial applications of colloids.

16

An Atom—What Is It?

198 As Dalton Saw It

The idea of the fundamental and indivisible atoms which the Greeks supposed constituted matter was revived in a more exact form by Dalton in 1804, mainly because of his investigation of the constancy of composition of chemical compounds. Thus when iron and sulfur unite to form two compounds (which we represent by FeS and FeS_2), a check on the quantities of these elements will show that in FeS every 56 grams of iron will require 32 grams of sulfur, whereas in FeS_2 64 grams of sulfur ($= 2 \times 32$) are necessary for the same weight of iron. Sulfur, then, though uniting differently in each instance, shows a simple multiple relationship of 32 and 64, or 1:2. Because to Dalton this could be only if there were unit quantities of sulfur, and hence of other elements, he conceived the necessity of these ultimate subdivisions, which he declared to be *atoms*.

199 Avogadro Draws a Distinction

Unfortunately Dalton did not make it clear that atoms are the ultimate chemical subdivisions, for he thought of atoms of compounds as well. We know now that many elementary gases, such as oxygen, nitrogen, hydrogen, are found existing in the form of pairs of their atoms. And it was Avogadro who in 1811 drew attention to the desirability of using the word *molecule* to describe the smallest particle of a compound which could exist alone. Under this term he included the elementary gases as well as compounds made up of different elements. In spite of its simplicity and necessity, this suggestion was not actually accepted until revived and re-affirmed by Cannizzaro several years later.

200 Prout's Disconcerting Influence

During this controversial period the relative weights of the elements as found from their combination with one another were accurately determined by a number of workers. These weights might correspond to the actual atomic weights or they might not, depending on the valence; but the concept of valence had not then been advanced. Several systems of weights were proposed based on the lightness of hydrogen by comparison with all other known elements. If hydrogen were taken as unity, all the other elements were found to be relatively large multiples of one—many, of course, with fractional values, for example, calcium, 40.07, and mercury, 200.61. It was Prout who, at this time, proposed his hypothesis that all the elements are multiple aggregations of hydrogen, thus inferring that fractional values for the atomic weights represented experimental inexactitude. But this hypothesis was unpopular and temporarily discarded.

201 Electricity Becomes a Factor

About this time Davy and Berzelius electrolyzed salts both in aqueous solution and in the fused state, preparing the pure metals copper, calcium, potassium and sodium. This use of a direct current of electricity led Berzelius to propose his dualistic or electrochemical theory, that elements are composed of two kinds of

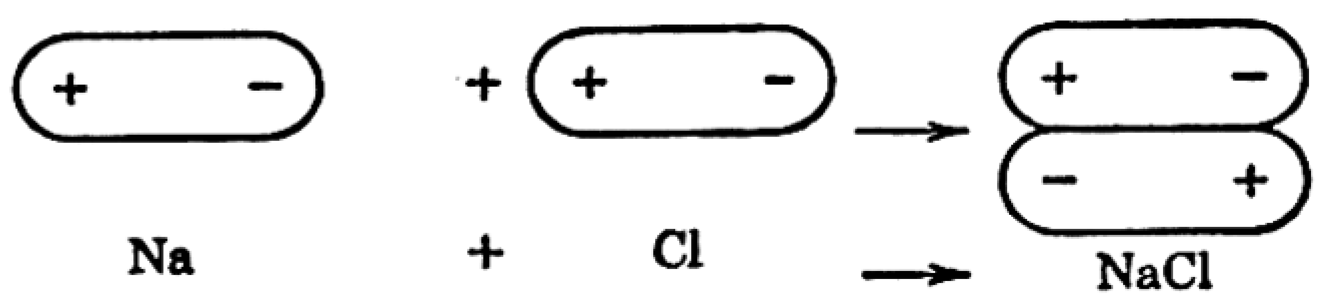


FIG. 54. The Berzelius atom consisted of unbalanced quantities of negative and positive electricity. The union of the two atoms, therefore, balances these charges to produce a stabler molecule.

electricity. Faraday had already named the poles of electrical batteries (voltaic cells) positive (to show whence he thought the current went out) and negative (to show whither he thought the current returned). According to Berzelius' theory, the atom of sodium possessed a large supply of positive and a small supply of negative electricity. Conversely, chlorine contained a small amount of positive electricity and a large amount of negative. Figure 54 will help to visualize the union between sodium and

chlorine. Faraday's researches into the deposition of metals by the electric current gave added emphasis to this theory by Berzelius, for he found that a definite quantity of electricity (96,500 coulombs) would deposit a quantity of any metal equal to its combining weight in grams; thus the electrochemical idea had a quantitative as well as a qualitative aspect. The consequences of this theory have never been discarded in their entirety, though the theory has changed with the passage of time.

Acceptance of the atomic and molecular theories about the middle of the nineteenth century clarified the relationships existing among atomic and combining (or equivalent) weights and valence in accordance with the simple statement that for any element the atomic weight = combining weight × valence.

202 Arrhenius Explains

In 1887 Arrhenius proposed his (at first) none too acceptable theory of electrolytic dissociation, now called more simply the ionic theory. This theory postulated the systematic break-up, either partial or complete, of acids, bases and salts in aqueous solution into electrically charged particles which Arrhenius called ions (wanderers). These ions received their charges at the moment of the molecular break-up, one ion getting some excess positive electricity, the other getting an equal excess of negative. The obvious conclusion is that the atoms of the neutral, unbroken molecule must have contained these electrical entities of opposite sign. Under Arrhenius' theory, valence became definitely associated with the electrical charge on the ions.

203 X-rays

In 1895 Röntgen discovered X-rays (also called Röntgen rays) and, shortly after, Becquerel found that a salt of uranium gave forth a radiation (γ-rays) that affected the photographic plate in the same manner as X-rays. This discovery caused a host of investigators to turn their attention to this new property of matter. It was later found that X-rays and γ-rays were similar; but whereas the latter were produced by the automatic decomposition of certain atoms, the former could be produced artificially by the passage of the electric current. These two developments progressed side by side, involving such names as the Curies, Perrin, J. J. Thomson, Crookes, Rutherford, Millikan and Moseley, to men-

tion a few of the pioneers in the field. From their work we can pick out certain experiments whose results have been of most interest to the chemist, leaving the rest of this extensive field to the physicist.

204 The Electron

When any of the common gases are sealed up at a pressure of about 0.01 mm in a glass tube fitted with metal electrodes, an electric discharge will pass through the tube and cause it to glow if

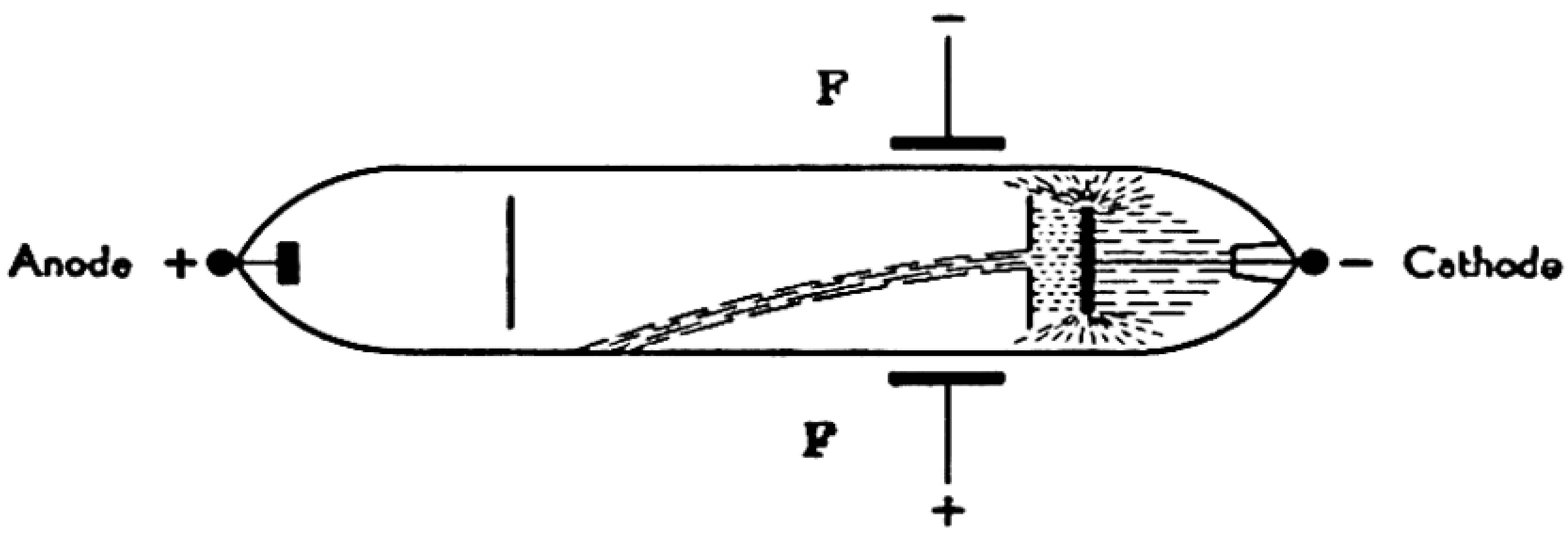


FIG. 55. Sir J. J. Thomson's cathode ray tube. Here electrons, shot away from the cathode, pass through a slit. This pencil of rays may be bent by the electrostatic field *FF* to show that electrons are negatively charged particles of electricity.

the electrodes are connected to a suitable source of electricity. At reasonably high gas pressures the discharge takes the form of a thin sparklike ribbon down the tube (Fig. 55). If a bar magnet or electromagnet is brought near such a tube the glowing ray is easily seen to be deflected by the magnetic field. Since these rays apparently originate at the cathode they are called *cathode rays*. By taking advantage of their deflection in a magnetic field, Perrin, in 1895, was able to show that cathode rays are made up of a stream of negatively charged particles.

It is shown in electromagnetic theory that if a particle with electric charge e and mass m is shot through a uniform magnetic field with uniform velocity, it will be deflected in a circular path. By measuring the radius of the path and controlling the other variables, the ratio of charge to mass e/m may be measured. J. J. Thomson (1897) employed this method to measure e/m for cathode rays and found it to be 1.2×10^8 coulombs per gram. Better recent measurements give 1.772×10^8 coulombs per gram. Various workers in Thomson's laboratory soon measured the approximate

value of the charge *e* for these particles and later Millikan measured it with high precision by means of his classical "oil drop experiment." When both *e* and e/m are known precisely, *m* can be calculated; it turns out to be about 1/1850 of the mass of a hydrogen atom. The cathode rays were thus shown to be streams of negatively charged particles of mass about 1/1850 that of the hydrogen atom. These particles were called negative electrons or just *electrons*, and atoms could no longer be considered the ultimate particles of matter.

205 Positive Rays

The electrons of the cathode rays are not the only moving particles in a gas-conducting electricity. Because of the influence of

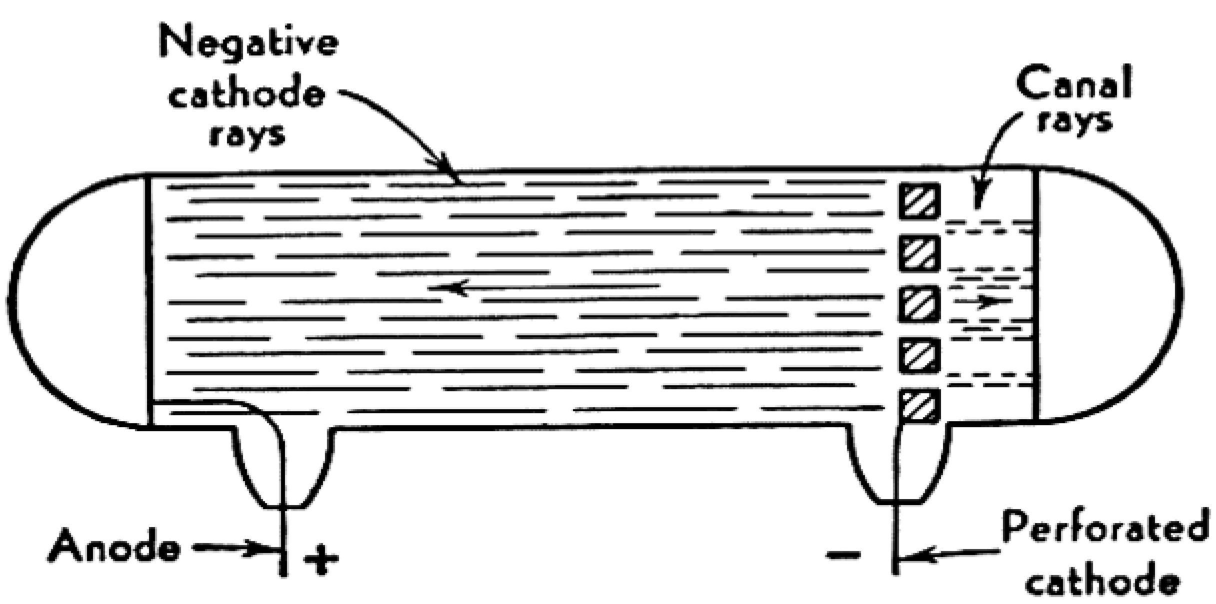


FIG. 56. Sir William Crookes's experiment where atoms, denuded of one or more electrons, pass through openings in a perforated cathode to be studied as to their mass and charge.

the electric field, the electrons acquire high velocities, and when they collide with neutral molecules of the gas in the tube, their energy is sufficient to knock electrons out of the gas molecules, leaving them with a positive charge. The positively charged molecules are immediately repelled by the anode and attracted by the cathode so that they, too, soon acquire high velocities. If a small hole is made in the cathode some of these positive rays will shoot through the perforation and may be studied in the space behind the cathode (see Fig. 56). These positively charged particles are deflected by electric and magnetic fields much as the cathode rays are, and this fact is made use of in measuring their mass and charge. It is found that the positive rays (sometimes called Canal rays) are made up of positively charged atoms as would be expected from their mode of formation. Thus, if the gas in the tube is oxygen,

the particles are atoms of oxygen that have lost one or more electrons; if the gas is hydrogen, they are hydrogen atoms stripped of an electron, and so forth.

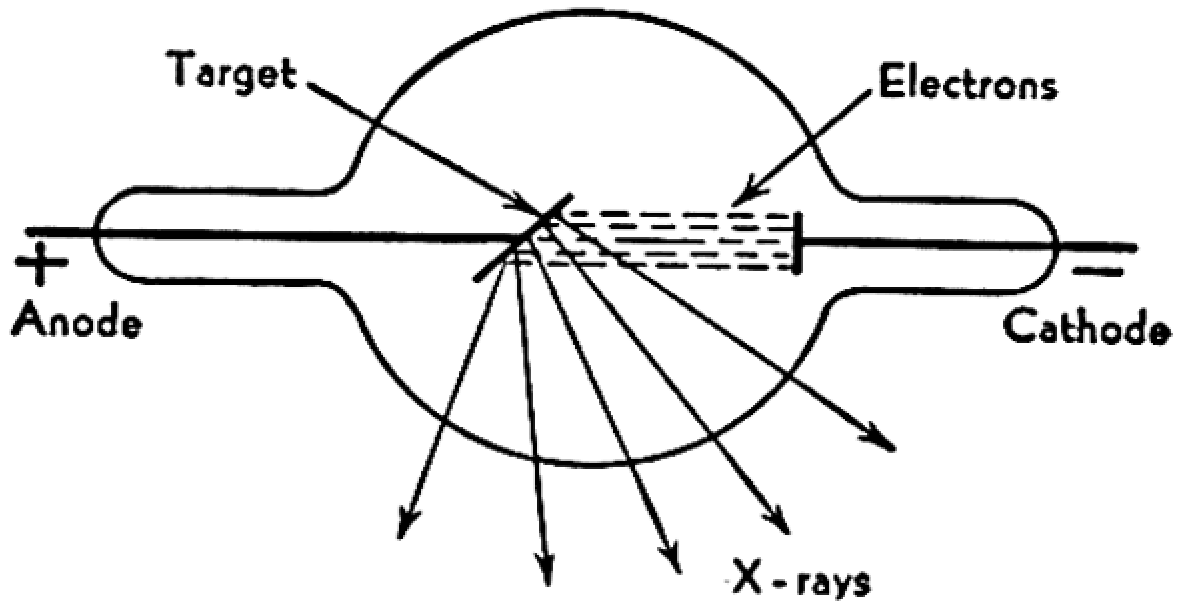


FIG. 57. A stream of electrons is shot from the cathode to a positively charged target. When they strike, X-rays are emitted.

Röntgen's discovery was in the use of a modification of the Crookes tube, where the cathode was so constructed (Fig. 57) that its rays converged and struck an oblique target (called the "anti-cathode") of some dense metal. By this means X-rays of high penetrating power are produced. X-rays, like γ-rays (see Fig. 58), are not deflected by a magnetic or electrostatic field and are therefore not charged. Actually X-rays are of the same general nature as light, but their wavelength is shorter.

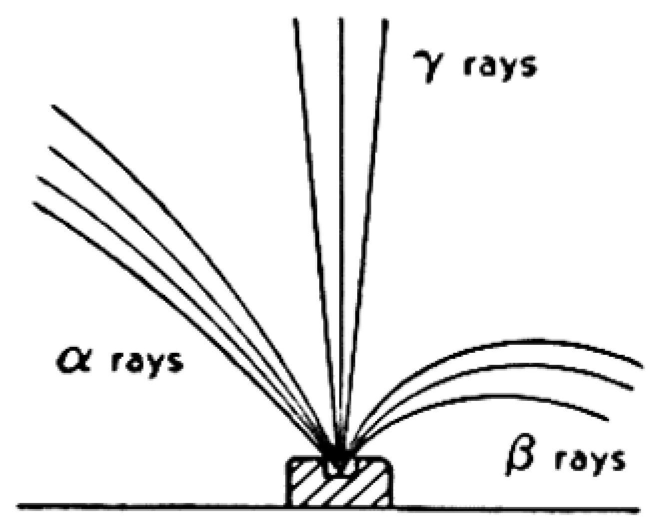


FIG. 58. Diagrammatic sketch of radioactive disintegration of radium, showing the positively charged alpha particles and negatively charged beta rays attracted by an electrostatic field while the uncharged gamma rays go straight outwards.

206 Rutherford's Nuclear Atom

When radioactive substances disintegrate they emit, among other things, particles called alpha particles. They were shown by Rutherford and his collaborators to be helium atoms that have lost two electrons and hence have two natural units of positive charge. The α-particles are shot off at speeds high enough to penetrate a considerable depth of air or metal foil. Rutherford and Chadwick found that when metal foil is bombarded with a beam of α-particles not merely does the ray pass straight through but the charged helium atoms are deflected and scattered at all angles in a way that could only be interpreted as indicating that

the metal atoms in the foil are not uniform but consist of a small positive nucleus surrounded by a cloud of electrons (Fig. 59). This conclusion is abundantly verified by the scattering of α-particles in air and other gases, for the high-speed particles can apparently pass right through many thousands of atoms and molecules before it hits the small nucleus of one squarely enough to be deflected. Then it may rebound in any direction, much as a stone will when thrown vigorously at a stony beach.

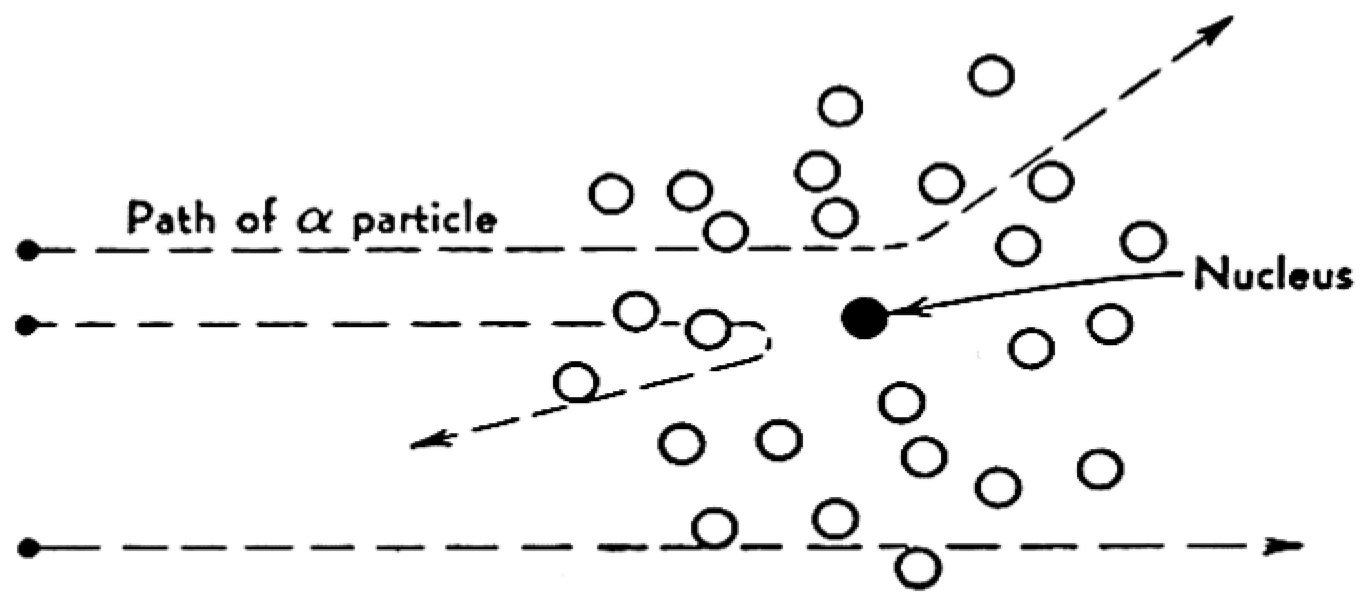


FIG. 59. Representation of an alpha particle bombarding an atom.

Radioactive substances continuously emit three types of rays:

(1) *Alpha rays* (α-rays) are atoms of helium thrown off in straight lines with velocities about one tenth that of light. These particles of matter carry two units of positive electricity, that is, each atom of helium has lost two electrons.
(2) *Beta rays* (β-rays) are electrons shot off in straight lines with velocities approaching that of light.
(3) *Gamma rays* (γ-rays) are electromagnetic vibrations identical with short X-rays.

The character and properties of these rays have been learned mainly by studying their behavior in electric and magnetic fields and by measuring their ability to penetrate air and other substances. For instance, in a strong magnetic field, α-rays are bent oppositely to β-rays, and γ-rays are not bent at all, showing that the charges are of opposite kind to α- and β-rays while γ-rays are not charged particles at all but electromagnetic vibrations.

When a radium atom (atomic weight 226) disintegrates, it loses one α-particle and becomes the inert gas radon (atomic weight 222). The α-particle quickly picks up two electrons and becomes a neutral helium atom. Thus the primary decomposition products of radium are helium and radon gases.

From an exhaustive study of atoms of the elements, both by observing those naturally radioactive and by bombardment of other elements, the conclusion has been reached that any element is made up of two parts, namely, electrons and the nucleus. The nucleus is composed of units of the hydrogen nucleus (the *proton*), which has the mass of the hydrogen atom, and the *neutron*, which is a neutral particle with the mass of the hydrogen atom. We know that *positrons* exist as well within the nucleus, though their function at the moment is not at all clear; they are the positively charged analogues of the electron. The contributions of Moseley, Bohr, Aston, Chadwick, Lawrence and others to the knowledge of the interior of the atom shows that it is electrically neutral, since the total positive charge on the nucleus is counterbalanced by a series of electrons wandering outside in regular orbits. Also, while the mass of the atom is concentrated in the nucleus, it is the arrangement of the electrons, and only the electrons, which determines the chemical behavior of an element.

207 Valence and Atomic Number

Hydrogen has the simplest atom, which is shown in Fig. 60 to possess the simple proton (or hydrogen ion) nucleus with one electron on the outside which travels around the nucleus much as the earth revolves about the sun. This external electron is extranuclear or orbital and constitutes the *atomic number* of the hydrogen atom. Similarly, all extra-nuclear electrons of the atoms of all elements give rise to the atomic numbers of those elements. Just so long as these electrons balance the positive charge of H, it matters little from the chemical point of view what the mass of the nucleus is. It thus becomes possible for atoms to behave similarly, having different masses in their nuclei. This situation gives rise to isotopes, as we shall see later.

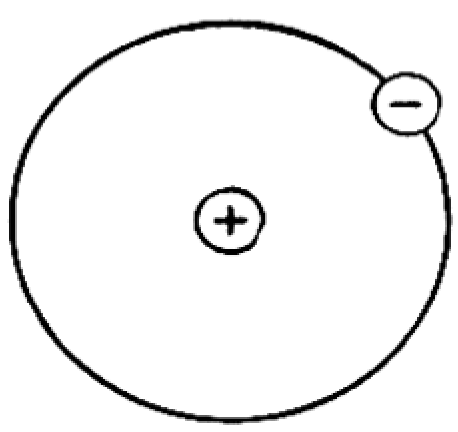


FIG. 60. The hydrogen atom consists of a positively charged nucleus called the proton, about which revolves a single electron.

In hydrogen, the proton is about 1850 times as heavy as the electron and therefore is responsible for the mass of the atom. The diameter of an electron is about 4×10^{-13} cm, and that of the proton is about 2×10^{-16} cm, the whole atom being about 2×10^{-8} cm in diameter. These dimensions are difficult to visualize,

but they mean that a tiny electron is whirling about a much tinier and heavier proton at what is really a vast distance away, and that the proton itself must be an enormously congested and heavy entity. Such visions of vacuity have been compared—and not too indifferently—to the solar and planetary systems of the celestial sphere, and they force upon us the idea gained from the study of gases that ordinary bodies are after all mainly space.

208 Hooking Up the Atoms—Valence

The most important chemical concept of the nineteenth century was valence, and in this respect the arrangement of the electrons about a nucleus gives a clue to the fundamentals of chemical

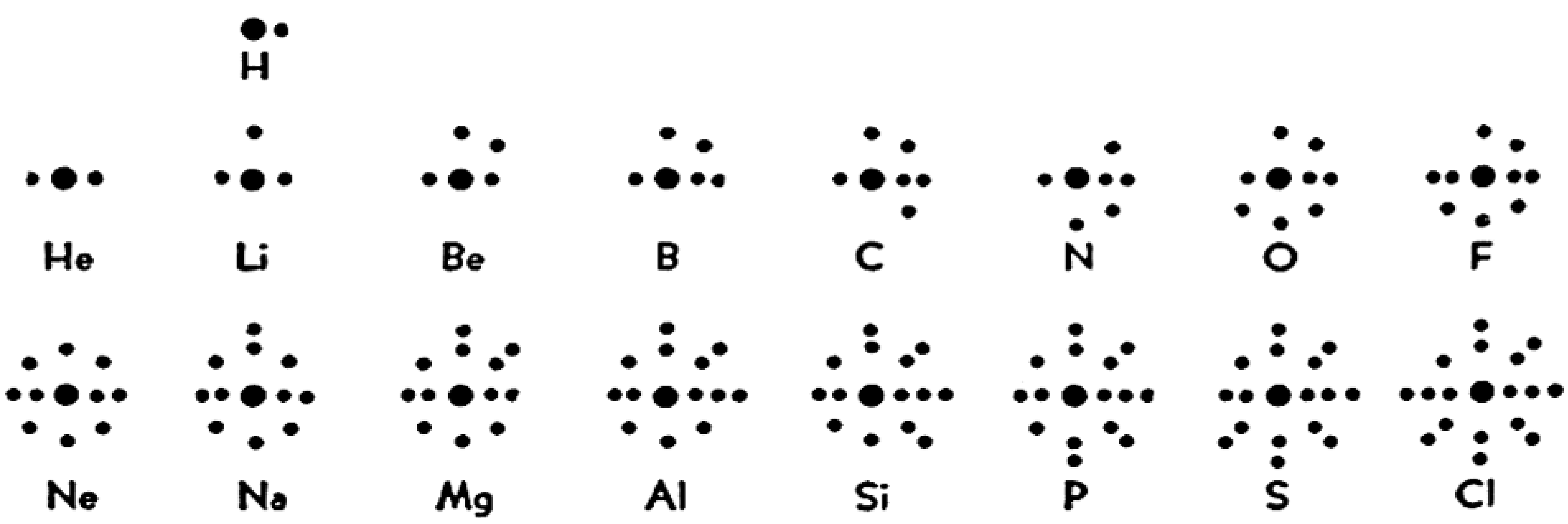


FIG. 61. Static representation of electrons arranged in concentric shells around the atomic nucleus.

combination. J. J. Thomson suggested on the basis of classical mathematics that the electrons must be grouped about the nucleus, and Bohr conceived of concentric shells, each containing a certain number of electrons, not unconnected with the groups of the Mendelejeff system (§ 216).

If, for the sake of convenience, we forget that these electrons are rotating in well-defined orbits and regard the atom as made up of a number of static parts, we get the following picture. In the hydrogen atom the lone electron is in a shell nearest to the proton nucleus; in helium, the next element of atomic weight 4 and atomic number 2 (that is, the number of electrons not attached to the nucleus directly), these two electrons are in the first shell; in lithium, of atomic weight 7 and atomic number 3, two electrons are in the first shell and one in an outer shell; beryllium (or glucinum) next, with atomic number 4, has two electrons in the inner shell and two in the outer shell. The electrons in helium in the inner shell show no valence whereas those in the outer shell show monovalence for lithium, divalence for beryllium, etc., in accordance with the

valence of the groups in the periodic table and as shown in Fig. 61. As we continue, we find neon, with an atomic number of 10, having two electrons in the inner shell and eight in the outer shell. If an outer shell is assumed to have a full complement when it possesses eight electrons, neon will be inert like helium. The next element sodium, with atomic number 11, will have two electrons in the innermost shell, eight in the next and one in an outer and new shell. This would accord monovalence to sodium, in agreement with the periodic system. It is a very clever scheme and is of enormous help, but it should be remembered that its usefulness does not confer on it the certainty of fact.

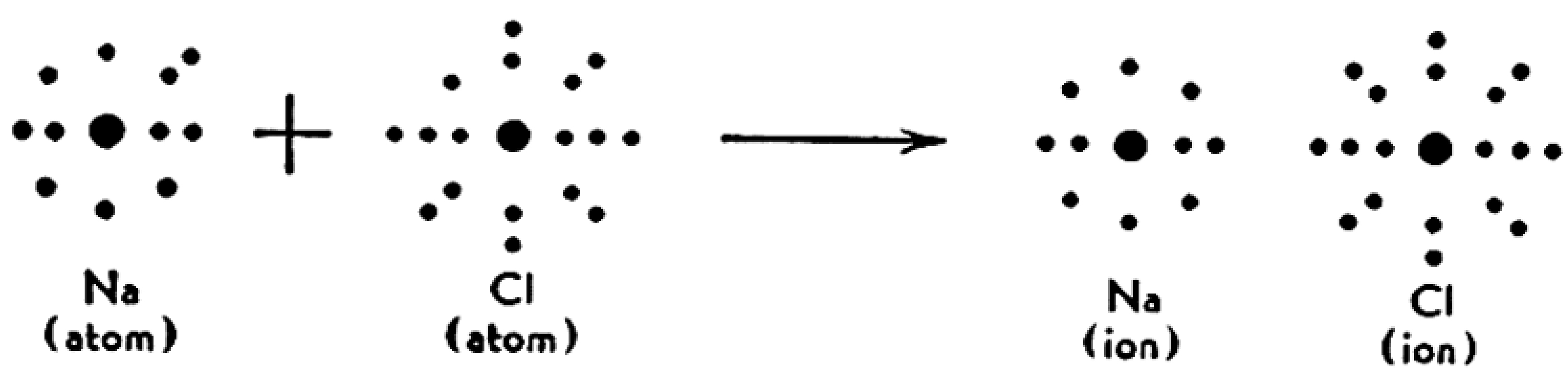


FIG. 62. The sodium atom donates its valence electron to a chlorine atom to form sodium and chlorine ions.

Various properties of atoms are associated with these electrons, but it is the number in the outermost orbit or shell in Fig. 61 which interests the chemist, for these numbers correspond to the valence. Thus, neglecting the inner shells, we can see how sodium forms a stable compound with chlorine, for a shell containing eight electrons would appear to represent chemical stability (Fig. 62). Moreover, the ionization of sodium chloride would result in a sodium atom wandering without its external electron, and being therefore positively charged; and in a chlorine atom with an electron too many, being thereby negatively charged. Note that the terms positive and negative are merely conventional and not used in the algebraic sense. The passage of an electric current, therefore, becomes a movement of electrons, though in the direction opposite to that envisaged by Faraday.

209 The Lewis-Langmuir Hypothesis

If the number of electrons in the outermost shell is eight and if it is assumed that a shell of eight electrons contributes to chemical stability or even to inertness as with the rare gases, the close juxtaposition of electrons of separate atoms to form such a shell should represent compound formation. This is in essence the hypothesis as put forward by G. N. Lewis and Langmuir, and independently

by Kossel, in the years 1916–1919. This stable grouping of eight electrons they called an octet. In their scheme those elements having one to three electrons in the outer shell could give them up readily to elements whose outer shells contained five to seven electrons, in order that the atoms so linked might each be surrounded by eight electrons. This hypothesis does not imply that the static arrangement which resulted from such combinations represented the actual arrangement in the molecule, but it has been of great assistance in promoting a visual conception of the workings of valence in chemical compound formation.

210 Uses of Electronic Formulae

One of the uses of electronic formulae is to visualize chemical combination, for example, in the union of hydrogen and oxygen to form water:

$$\mathrm{H\cdot + H\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}\cdot \rightarrow H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H} \tag{87}$$

Here the six planetary electrons of oxygen become the stable number eight by the addition of the two electrons from the two hydrogen atoms. In the union of sodium with chlorine to form the ionizing salt sodium chloride:

$$\mathrm{Na\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow Na:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:} \tag{88}$$

On ionization the sodium ion, which is the sodium atom minus its electron, wanders around in aqueous solution with a unit excess of positive electricity, or Na^+ as it is commonly represented because it has lost one electron. Meanwhile the chlorine ion, which is merely the chlorine atom with an extra electron, appears with a negative charge, or Cl^-. This transfer of the lone outermost electron of sodium to fill the outer shell of chlorine gives rise to the type of valence called *electrovalence.*

Distinct from this type is a second known as *covalence,* in which the electrons are not donated but shared as in the compound methane:

$$\mathrm{\cdot\underset{\cdot}{\overset{\cdot}{C}}\cdot + 4H\cdot \rightarrow \begin{array}{c} H \\ H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{C}}:H \\ H \end{array}} \tag{89}$$

a distinction which differentiates non-ionizing compounds from those like sodium chloride.

A third type similar to covalence is known as *coordinate covalence*, examples of which are beyond the scope of this course.

All metals tend to enter solution as ions, but some show this tendency more than others, that is, show a greater solution pressure. These metals are rated according to their tendency to lose electrons and become ions by comparison with hydrogen. Potassium thus develops a greater electromotive force than hydrogen, and copper a smaller one. The result of these differences will cause (1) a piece of iron to enter solution as ions and displace copper ions, the latter being precipitated as neutral particles; (2) a flow of electrons from the iron to the copper if both metals are dipped into an acidic solution and joined outside the solution by wires; and (3) iron to liberate hydrogen from a dilute acidic solution whereas copper will not do so. Thus the elements have been arranged in the decreasing order in which they tend to give up electrons. It is called the electromotive series of the elements and is shown in part in Table 11.

TABLE 11

ELECTROMOTIVE SERIES OF THE METALS

Lithium	(Li)	Nickel	(Ni)
Potassium	(K)	Lead	(Pb)
Sodium	(Na)	Tin	(Sn)
Magnesium	(Mg)	Hydrogen	(H)
Aluminum	(Al)	Copper	(Cu)
Zinc	(Zn)	Silver	(Ag)
Iron	(Fe)	Gold	(Au)
Cadmium	(Cd)		

211 Isotopes

The radioactive disintegration of an atom, for example, radium, with loss of mass will eventually place some of the products in the same position as that occupied by some other element with the same atomic number but with a different atomic weight. Such elements are called isotopes.

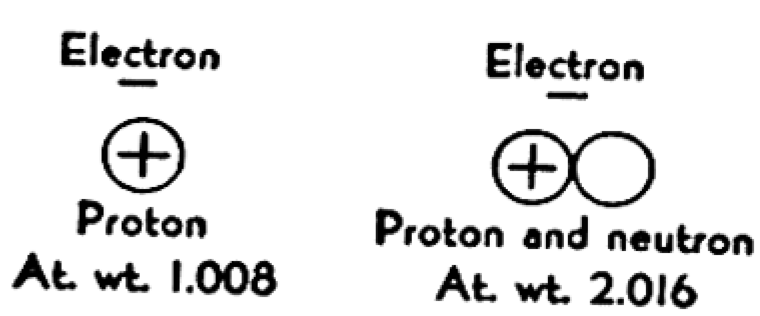


FIG. 63. "Light" and "heavy" hydrogen.

We now know of isotopes of nearly all the elements. Hydrogen (atomic weight 1.008) has its deuterium (atomic weight 2.016); and there are three known neons of atomic weight 20, 21 and 22 which together show a mean atomic weight of 20.2.

212 Artificial Radioactivity

During the bombardment of the element boron with alpha particles, Irène Curie (daughter of the famous Curies previously mentioned) and Joliot were able to show that the neutrons so produced gave rise to nitrogen atoms that were radioactive; this was called *radionitrogen*. This nitrogen is chemically very similar to ordinary nitrogen as we have studied it. After this artificial production of a radioactive element, others were rapidly discovered (by the bombardment method) by Lawrence and Henderson, using deuterons, the positively charged nucleus of heavy hydrogen. The best means for producing radioactive elements by bombardment was devised by Lawrence of California. It involves use of an instrument known as a cyclotron, having a weight of many tons. Here deuterons are made to travel in a circular space in a magnetic field, picking up energy with each cycle until they reach a pitch of 200 million volts. They are then ready to be directed on to the target that has been chosen to produce the desired radioactive element.

This creation at will, and under the impact of fast-moving particles, of unstable and hence radioactive nuclei is called *artificial radioactivity*. If we regard the nucleus of an ordinary element. therefore, as stable, the high-powered bombardment of it by neutrons, for example, increases the mass of that nucleus to produce temporarily a new and highly unstable nucleus of greater mass (atomic weight). In time this unstable nucleus may rearrange to a stable configuration, perhaps losing one or more of its component parts, namely, neutron, proton, electron or positron, thus demonstrating its similarity to naturally occurring radioactive elements like uranium or radium.

Since 1940 new elements have been synthesized having atomic numbers 93, 94, 95 and 96, that of uranium being the highest previously known (92). They have been given the names neptunium, plutonium, americum and curium. There would appear to be no limit to researches along this line.

213 Summary

The hydrogen atom is the simplest of all atoms; it consists of a nucleus called the proton. This proton is very small, very heavy and positively charged electrically. Around this proton revolves a particle called the electron, in mass one eighteen hundred and fiftieth of the proton (1/1850), and with a unit charge of negative electricity.

Other atoms consist of a heavy nucleus and a number of electrons surrounding it. Within the nucleus are (1) neutrons (the equivalent of neutral hydrogen atoms), (2) positrons (the positively charged counterpart of the electron) and (3) protons. In concentric orbits around the nucleus is a number of electrons corresponding to the number of free protons within the nucleus; this number is called the atomic number.

The number of electrons in the outermost orbit controls the chemical behavior of an element. The arrangement of the different constituents within the nucleus determines density and other properties of a physical kind.

Valence electrons appear either (1) to be given up to other atoms resulting in the formation of ions or (2) to be shared between atoms. These two main kinds of behavior are called electrovalence and covalence respectively.

The nucleus of an atom is chemically less important than the external electrons, but an unstable arrangement within the nucleus produces radioactivity or radioactive disintegration. As long as the atom possesses the same external configuration of electrons its chemical behavior will be the same; a change in nuclear mass produces actually different elements with the same chemical reactions. Such elements are called isotopes.

Radioactive disintegration throws off positively charged atoms of helium and (negatively charged) electrons accompanied by non-material gamma- or X-rays.

Unstable nuclei may be produced by bombardment with, for example, fast-traveling neutrons. If such an unstable nucleus rearranges itself without loss of matter, an isotope is produced. If, however, a loss occurs, a radioactive nucleus has been produced temporarily. It is therefore possible by suitable bombardment (1) to break down a hitherto stable atom and (2) to build up a heavier atom. This is real transmutation—such as was long sought by the alchemists.

Our knowledge of atomic constitution has been built up slowly by one discovery after another, chiefly in the realm of physics, where disintegration particles were found to resemble the products of high voltage electrical discharges in gases.

Matter is therefore entirely electrical in its analysis to date; in other words, all matter ultimately is a manifestation of energy. So far we have not succeeded in creating matter out of energy; but in nature matter is being continuously destroyed with the production of energy. Although for all chemical purposes the law of conservation of mass is still valid, in the final analysis the law of conservation of energy stands alone.

Questions

1. Show in outline the development of atomic structure from Dalton's first concept of the atom to the present time.
2. Define atom, ion, proton, electron, neutron, positron, isotope.
3. What part of the atom controls its chemical behavior?
4. Of what chemical importance is the nucleus?
5. What kinds of valence have you met?
6. What do you understand by radioactive disintegration?
7. Of what importance is a synthetically formed nucleus?

17

The Periodic Classification of the Elements

214 Correlation of the Elements

Since chemistry deals with the properties of some ninety elements and since a great deal of information has been accumulated about each one, it must appear at once that a prodigious strain is placed upon the memory of anyone who attempts to obtain a comprehensive knowledge of the subject. Fortunately it is possible to group these elements into a small number of families so that each member of any one family will show properties, both physical and chemical, which are shared by other members of the same family.

The first really useful step in this direction was taken by Döbereiner, who listed together what he called *triads of elements*. We may pick such examples of three-of-a-kind in the non-metals chlorine, bromine and iodine, and the metals lithium, sodium and potassium, or calcium, strontium and barium.

215 Newlands and His Law of Octaves

Döbereiner's system tended towards isolating such triads, and a more rational scheme was put forward by Newlands. His scheme was to write down the known elements (exclusive of hydrogen, the lightest) in increasing order of their atomic weight. In this way he showed that the eighth element in his list strongly resembled the first, the ninth the second and so on. This scheme, known as Newlands' law of octaves, is represented below, with the symbols of the elements concerned being used:

Li	Be (Gl)	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

A very little study of the physical and chemical properties of the elements vertically placed will show how closely they resemble each other. But Newlands' system failed chiefly because in his complete formulation he did not allow for elements which were unknown to him and have since been discovered. An excellent analogy is found in the white keys of a properly tuned piano, where a distinct harmonization is noticeable between C and C_1, say, which is quite different from the effect produced by striking C and B simultaneously. Similarly lithium and sodium have very similar reactions, whereas sodium and chlorine are distinctly antithetical, both physically and chemically.

216 Mendelejeff and His System

Finally, in 1869, Mendelejeff, a great Russian scientist, set forth the principles of our present scheme as follows: *The properties of the elements are a periodic function of their atomic weights.* This is known as Mendelejeff's periodic law. Its practical meaning is this. If the elements are written horizontally in increasing order of their atomic weights, it is possible at intervals to take a number of elements in a straight line and place them vertically underneath the previous ones.

The elucidation by Moseley of the electronic charges of the atoms showed that Mendelejeff had placed his ultimate emphasis on the weight of the atom rather than on the number of electrons associated with that atom. The substitution of the atomic numbers for atomic weights is of considerable significance. It involves the conception of an atom as a bundle of electrical charges, whereas the atomic weight refers to the entire atom, of which the heavier part by far is the positive nucleus.

217 The Periodic Table

On page 197 is the full periodic table, but for the present the following simple arrangement by groups will suffice:

			H				
0	I	II	III	IV	V	VI	VII
He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl
..	K	Ca	..	..	..	..	Br
..	..	..	..	..	..	..	I

Omitting hydrogen, we have two horizontal lines (called series) of elements, each one of which differs considerably from the ones to the left and to the right of it. But we also have eight vertical sets (or pairs, in this brief table), and the elements of each pair are very similar in both physical and chemical properties. These vertical sets are called groups and are numbered from zero to seven in Roman numerals.

The numbering of these groups is interesting. From left to right and from top to bottom the atomic weight increases as Mendelejeff required; and so it happens that the elements of Group 0 have no valence, the valence of the elements of Group I is one, of Group II is two and so on.

TABLE 12

THE FIRST (HORIZONTAL) SERIES

No. of Group	0	I	II	III	IV	V	VI	VII
Element	He	Li	Be	B	C	N	O	F
Atomic Weight	4	6.94	9.02	10.8	12	14	16	19
Hydride	..	LiH	BeH_2	B_2H_6	CH_4	NH_3	H_6O	HF
Valence (to H)	0	1	2	3	4	3	2	1
Oxide	..	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	..	..
Valence (to 0)	0	1	2	3	4	5	..	..

This series shows three interesting transitions from left to right: (1) increase in atomic weight, (2) increase in valence (in combination with oxygen) and (3) increase in valence (in combination with hydrogen) up to 4 and then a regular drop back to 1. The second series (from A to Cl) shows (1) and (3) as above, but (2) goes from 0 to 7, because of the compounds SO_3 and Cl_2O_7.

We can now extend the previous table to include these figures:

Group Number	0	I	II	III	IV	V	VI	VII
Valence (to hydrogen)	0	1	2	3	4	3	2	1
Valence (to oxygen)	0	1	2	3	4	5	6	7

This valence to oxygen is the maximum valence. For example, sulfur in VI unites with hydrogen to form H_2S (valence = 2), with oxygen to form SO_2 (valence = 4) and again with oxygen to form SO_3 (valence = 6).

Any element in Groups V, VI and VII may therefore show several valences; but the full satisfied valence is 5, 6 and 7, though

THE PERIODIC TABLE

(After Mendelejeff and brought up to date.)

The atomic number appears above the symbol for each element and the atomic weight below; dots indicate either an undiscovered element or one whose atomic weight is undetermined.

Group	0	I		II		III		IV		V		VI		VII		VIII		
Subgroup		A	B	A	B	A	B	A	B	A	B	A	B	A	B			
Oxide and Hydride		R_2O	RH	RO	RH_2	R_2O_3	RH_3	RO_2	RH_4	R_2O_5	RH_3	RO_3	RH_2	R_2O_7	RH			
	2 He 4.003	1 H 1.008 3 Li 6.94			4 Be 9.02		5 B 10.82		6 C 12.01		7 N 14.008		8 O 16.0		9 F 19.0			
	10 Ne 20.18	11 Na 23.0			12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.066		17 Cl 35.46			
	18 A 39.94	19 K 39.1	29 Cu 63.54	20 Ca 40.08	30 Zn 65.38	21 Sc 45.1	31 Ga 69.72	22 Ti 47.9	32 Ge 72.6	23 V 50.95	33 As 74.91	24 Cr 52.01	34 Se 78.96	25 Mn 54.93	35 Br 79.916	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
	36 Kr 83.7	37 Rb 85.48	47 Ag 107.88	38 Sr 87.63	48 Cd 112.41	39 Yt 88.92	49 In 114.76	40 Zr 91.22	50 Sn 118.7	41 Cb 92.91	51 Sb 121.76	42 Mo 95.95	52 Te 127.61	43 Ma ..	53 I 126.92	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
	54 Xe 131.3	55 Cs 132.91	79 Au 197.2	56 Ba 137.36	80 Hg 200.61	57–71 * Rare Earths	81 Tl 204.39	72 Hf 178.6	82 Pb 207.21	73 Ta 180.88	83 Bi 209.0	74 W 183.92	84 Po ..	75 Re 186.31	85	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
	86 Rn 222	87		88 Ra 226.05		89 Ac ..		90 Th 232.12		91 Pa 231		92 U 238.07						

* Rare Earth Elements														
57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il ..	62 Sa 150.43	63 Eu 152	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

the common valence may be 3, 2 and 1, respectively. Two systems are in use for describing the valence of an element. If the valence is 1, the adjective is composed of the prefix uni (*uni*, from Latin) or mono (*mono*, from Greek) followed by valent, as univalent or monovalent; if the valence is 2, bivalent or divalent, and so on. Usually both types of prefixes are used indiscriminately since both are known to the practiced chemist.

Here are two examples of the usefulness of the periodic table in making up formulae:

1. Sodium (monovalent) combines with oxygen (divalent) to form a simple oxide; the formula is Na—O—Na or Na_2O.

2. Aluminum (trivalent) and oxygen; the formula is Al_2O_3. It may be obtained by finding the least common multiple of 3 and 2, that is, 6. Then, dividing 6 by 3 (for Al) and obtaining Al_2, and dividing 6 by 2 (for O) and obtaining O_3, we have Al_2O_3. Also, thinking of valence in terms of bonds, aluminum needs at least 2 atoms of 3 bonds each (= 6) to hold at least 3 atoms of oxygen of 2 bonds each (= 6) so as to have no bonds left over. The application of this simple scheme is not infinite but is very helpful.

An interesting variation of the Mendelejeff system is the Harkins scheme, which shows the elements arranged consecutively about a cylinder, in the form of a helix, so that the groups still appear in their vertical setting. Though not so easy to use as the flat table, its principle of construction conveys the idea of continuity so important to the electrical concept of atoms.

THE PERIODIC TABLE—GROUP BY GROUP

218 Group 0—the Rare Gases

This, the first of the vertical families of the periodic table, is appropriately numbered since the six elements contained in it have no valence, that is, they form no known compounds either among themselves or with other elements. Because of their inability to form compounds they are sometimes called the *inert gases;* they are also called the *rare gases.*

Helium was discovered by a study of the spectrum of the sun long before it was found on earth. It occurs chiefly in the gas wells of Kansas and Texas, where it may constitute as high as 2 per cent of the natural gas. Since helium has very nearly the buoyant

power of hydrogen and lacks the inflammability of that gas, it is of great importance in the inflation of balloons.

Neon, argon, krypton and xenon occur to the extent of not more than 1 per cent in the atmosphere, from which they may be obtained by liquefaction and subsequent distillation. Neon is used in light bulbs because of the light it gives out under the influence of electricity. Radon is, together with helium, produced by the radioactive disintegration of radium.

TABLE 13

GROUP 0—THE RARE GASES

Name	*Symbol*	*At. Wt.*	*At. No.*
Helium	He	4.0	2
Neon	Ne	20.2	10
Argon	A	39.9	18
Krypton	Kr	82.9	36
Xenon	Xe	130.2	54
Radon	Rn	222	86

219 Group IA—the Alkali Metals

TABLE 14

GROUP IA METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr. (20°C)*	*M. Pt., °C*	*B. Pt., °C*
Lithium	Li	6.9	3	0.53	186	1336
Sodium	Na	23.0	11	0.97	97	880
Potassium	K	39.1	19	0.86	62	760
Rubidium	Rb	85.5	37	1.53	38	700
Cesium	Cs	132.9	55	1.9	26	670

Of the five metals shown above the first three are of most interest and, most particularly, sodium and potassium. Compounds of these two are common in natural deposits and are in general use, whereas lithium, rubidium and cesium have not been found in large quantities as yet. All five are soft, white metals and are readily oxidized by the atmosphere forming oxides with the general formula M_2O, where M represents the metal. They also react vigorously with water, liberating hydrogen and forming the soluble hydroxide according to the equation:

$$2M + 2H_2O \rightarrow H_2 \uparrow + 2MOH$$

It is because of the formation of alkalies that these metals have come to be known as the *alkali metals*. This reaction with water requires that they be kept away from water and the atmosphere, either in dry air-tight cans or under paraffin oil.

That there is a gradual change in properties going from the first to the last may be shown as follows. Lithium reacts vigorously but quietly with water, sodium more vigorously and potassium with such energy as to ignite the hydrogen simultaneously evolved. Lithium hydroxide (LiOH) is an alkali, as are also the other hydroxides. A comparison of the five, however, reveals that this is the weakest, the strongest being cesium hydroxide (CsOH), the others (NaOH, KOH, RbOH) having intermediate strengths in the order given. They are the strongest known alkalies as a class.

Table 14 gives further examples where the specific gravity increases regularly with atomic weight and the melting points and boiling points show a somewhat similar effect—but in the reverse direction, strange as that may seem.

These elements give rise to a multitude of chemical compounds in general use, of which the commonest and most used are those of sodium, whose chloride (common salt, NaCl) is the largest source of Group IA compounds in nature. Their compounds are uniformly very stable; hence the preparation of the elements requires the use of the electric current on their fusible hydroxides (§ 458). The presence of these elements in their compounds may be ascertained by the varied colors which they display when strongly heated; lithium, for example, emits a bright red, sodium a strong yellow, potassium a pale violet, rubidium a dark red and cesium a blue. They also form amalgams (alloys) with mercury very readily.

The commonest of these elements are, first, sodium and then potassium, and their nitrates, chlorides and carbonates are found widespread in nature. Sodium carbonate (Na_2CO_3), also known as soda ash or washing soda, enjoys a very large industrial use, as, for example, in softening water and in the manufacture of soap and glass. It is the most widely used of all sodium compounds. Two immense natural deposits of sodium carbonate exist, one in California and the other in British East Africa; yet most of the world's supply is obtained from the Solvay process, with common salt used as the starting point (§ 502). The natural sources of potassium salts are Germany and France, but Chile and South

Africa contain vast beds of sodium nitrate, frequently called Chile saltpeter to distinguish it from potassium nitrate long known as saltpeter (salt rock).

220 Group IB Metals

TABLE 15

GROUP IB METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt., °C*	*B. Pt., °C*
Copper	Cu	63.54	29	8.94	1083	2310
Silver	Ag	107.88	47	10.5	960	1950
Gold	Au	197.2	79	19.3	1063	2600

The elements copper, silver and gold do not show much resemblance to the alkali metals; indeed they have much more in common with zinc, mercury and platinum. Their physical properties as shown in Table 15 point to high specific gravity, melting point and boiling point. The last two properties do not show the gradation observed in Group IA; both copper and silver are harder than gold. Their resistance to corrosion is emphasized by all three being found free in nature under various conditions. In addition, gold is not easily tarnished except when attacked by the halogens and aqua regia. The latter is a mixture of concentrated nitric and hydrochloric acids, which, forming nitrosyl chloride ($NOCl$), attacks and dissolves gold to produce the chloride ($AuCl_3$). Since gold is so resistant to corrosion, is soft and extremely malleable (the most so of all known metals) and has a pleasing luster and color, it was known as a *noble metal* which could only be dissolved by a royal water.

Copper and gold are the only metals with distinctive colors, the others being variations of silver-white. Their hydroxides are insoluble in water and unstable, decomposing to the oxides, and cannot therefore be classed as alkalies. Copper salts are blue to green in varying depths of color, whereas gold and silver compounds are chiefly pale yellow or white.

Although these three metals are excellent conductors of heat and electricity, copper alone is cheap enough for such uses, silver and gold being kept for currency and for ornamental and decorative purposes. The hardness of copper makes it of use in alloys, especially in currency where a 10 per cent content will greatly increase

the life of gold and silver coins. Because of its great industrial importance in the manufacture of metal coatings, bronze (an alloy of tin) and brass (an alloy of zinc), copper is next to iron in the world's metal economy. It is very easily electroplated on other metals and serves as a base for the plating on of gold and silver, whose appearance is more popular and, in the case of gold, more resistant to tarnishing. Copper is found in many countries of the world, North America being the largest producer at the moment. Silver salts of the halogens find a large use in photography because of their sensitivity to light and subsequent color changes (§ 124).

Whereas the valence of the Group IA metals is always one, copper may be monovalent or divalent, silver monovalent and gold monovalent or trivalent. Largely because of these differences, compounds of these three metals form complex compounds with, for example, ammonia and potassium (or sodium) cyanide. Thus copper ammoniosulfate [$Cu(NH_3)_4SO_4$] is a solvent for cellulose, and potassium silver cyanide [$KAg(CN)_2$] and potassium aurocyanide [$KAu(CN)_4$] are employed in electroplating.

Special interest attaches to gold because it has been for a long time the standard of exchange in international trading. The world is producing gold to a value of about $950,000,000 annually. Because of her favorable trading position the United States of America has nearly $23,000,000,000 of gold stored under government supervision, which is equal approximately to all the gold mined in the world since this continent was discovered in 1492.

221 Group IIA Metals

TABLE 16

GROUP IIA ALKALINE EARTH METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Calcium	Ca	40.08	20	1.55	810	1488
Strontium	Sr	87.63	38	2.6	752	1383
Barium	Ba	137.36	56	3.5	850	1636
Radium	Ra	226.05	88	5	960	....

These elements are known as the *alkaline earths*; calcium is one of the commonest and radium one of the rarest. The first three are well known and resemble the alkali metals, being soft, white and of low specific gravity. They are divalent. All three react

with water to form the hydroxides, and liberate hydrogen. Their reaction, however, is not violent; the hydroxides produced are less soluble in water and are not so highly ionized as those of the alkali metals:

$$M + 2H_2O \rightarrow M(OH)_2 + H_2 \uparrow \tag{90}$$

They burn readily in air to form oxides with emission of brick-red, blood-red and green light, respectively. Lime or calcium oxide (CaO) was formerly used to emit a brilliant white light produced by playing a very hot flame on the lumps; hence the term *limelight*. The solubilities of salts of these elements are much less than their alkali metal analogues. The sulfates, carbonates, etc., which occur naturally, are insoluble; hence the name alkaline earths.

The two most important compounds of these elements are probably calcium carbonate ($CaCO_3$), found widespread as marble, chalk and limestone, and calcium phosphate [$Ca_3(PO_4)_2$]. The latter occurs in the earth's crust as phosphorite and is the source of phosphorus compounds and certain fertilizers; it also forms the bony structures of animals. Calcium carbonate, precipitated in a fine state of division from solution, is in demand as a constituent of polishes of various kinds. Similarly prepared barium sulfate ($BaSO_4$) finds use in the paint and paper industries.

With heating, limestone gives off carbon dioxide, leaving behind the oxide known as lime:

$$CaCO_3 \rightarrow CO_2 \uparrow + CaO \tag{91}$$

Carbon dioxide may be liquefied and used for making soft drinks, etc., and lime finds extensive application in the manufacture of various cements and as a fertilizer. Gypsum, a hydrated sulfate of calcium ($CaSO_4 \cdot 2H_2O$), is used in the manufacture of plaster of Paris ($CaSO_4 \cdot \frac{1}{2}H_2O$).

The rarity of radium limits its use in chemical reactions; it finds its greatest use in medicine.

222 Group IIB Metals

These elements, except mercury, which is a liquid, are all much harder than the alkaline earths. The specific gravities of beryllium and magnesium are low by contrast with the other three, and the high melting and boiling points of beryllium are significant. Magnesium, zinc, cadmium and mercury show a closer similarity

to copper, silver and gold than to calcium, strontium or barium. All are grayish-white in color and all mainly divalent (except mercury, which may also be monovalent). They form no compounds with hydrogen but react with oxygen to form oxides such as BeO and MgO. All their hydroxides, of the general formula

TABLE 17

Group IIB Metals

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °C	*B. Pt.,* °C
Beryllium	Be(Gl)	9.1	4	1.85	1282	2780
Magnesium	Mg	24.3	12	1.74	651	1110
Zinc	Zn	65.38	30	7.14	419.5	907
Cadmium	Cd	112.4	48	8.65	321	778
Mercury	Hg	200.6	80	13.6	−38.9	357

$M(OH)_2$, are insoluble in water. The preparation of magnesium is given on page 388.

Magnesium oxidizes readily in the atmosphere and, when incandescent, produces a light of high actinic value in photography and in flares. Many alloys are made from this subgroup, for example, magnesium with copper and with aluminum. The most recent of them is made with beryllium and aluminum, where the former increases the tensile strength of the latter enormously. Similarly, a trace of beryllium greatly increases the strength of copper.

Magnesium sulfate ($MgSO_4$), commonly known in the crystalline form as Epsom salts, occurs naturally in certain springs. However, the chief sources of the metal and its compounds are magnesite ($MgCO_3$) and dolomite (the mixed calcium magnesium carbonate), which occur very extensively in the earth's crust. Magnesium oxide finds great industrial application in furnace linings and in the building industry; the hydroxide [$Mg(OH)_2$] is used in various kinds of pharmaceutical preparations to counteract acidic conditions in the mouth and stomach. Certain hydroxy carbonates of magnesium find a use in the cosmetic industry, and in making heat insulators when mixed with the cheaper grades of asbestos.

Magnesium chloride ($MgCl_2$) is quite hygroscopic, and when in table salt makes it sticky and non-running, particularly in damp weather.

Zinc is used in the manufacture of galvanized iron; its oxide (ZnO) is a constituent of many paints and ointments.

Mercury (Hg; Latin, *hydrargyrum*) forms a great variety of compounds, such as the red and yellow oxides (HgO) used in eye salves, calomel (Hg_2Cl_2), a stimulant for the alimentary tract, and corrosive sublimate ($HgCl_2$), a deadly poison. The mercury vapor lamp, which operates by illuminating the vapor of mercury in the heat of the electric arc, produces a brilliant blue light that emits certain important wavelengths. Mercury resembles copper in that its compounds are poisonous. HgONC, mercury fulminate, is a well-known detonator for charges of explosives. The alloys of mercury have long been known as *amalgams*. Spain and Italy are the chief sources of mercury whereas North America is self-sufficient in the other metals of this group.

223 Group III Metals

This group contains a large number of elements, including the *rare earths*, as they are called. Among them are scandium, yttrium, lanthanum, actinium, gallium, indium, thallium and fourteen others of little commercial importance except cerium. Cerium is known chiefly for its alloys used in gas and tobacco lighters. The oxide CeO_2 glows brilliantly when incandescent and so finds use in the Welsbach gas mantle.

TABLE 18

GROUP IIIB METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Boron	B	10.8	5	2.45	2000	subl. 3000
Aluminum	Al	27	13	2.7	660	1800

Only two elements here, boron and aluminum, are of importance to us; both are trivalent. Neither occurs free in nature, and the only application of boron is by means of its compounds. The chief source of this element is borax ($Na_2B_4O_7$), found in great quantity in California. When dissolved in water it produces an alkaline solution of great cleansing power. It was formerly much more used than sodium carbonate, which it so much resembles. It finds considerable application in the manufacture of certain types of resistant glass. Boric (or boracic) acid (H_3BO_3) is used medicinally as a mild antiseptic, such as eye washes.

Though metallic aluminum has never been found free in nature, its compounds with oxygen, a number of other metals and silica (SiO_2) are found widely distributed in clays, feldspars, etc.

In 1886 the modern process for its manufacture from bauxite (Al_2O_3) in cryolite (Na_3AlF_3) was discovered by two independent investigators, Heroult of France and Hall of the United States, when both were about twenty-two years old. Since that time the growth of uses for the metals has been phenomenal.

224 The Preparation of Aluminum

Aluminum is prepared electrolytically from its oxide (Al_2O_3) in fused sodium aluminum fluoride (Na_3AlF_6). In the Hall process (page 389) the molten metal is run off from the bottom of the cell into molds, where it solidifies. The oxygen given off at the carbon anode gradually wears the anode away by oxidation to carbon monoxide:

$$Al_2O_3 \rightarrow 2Al \downarrow + 3O \uparrow \tag{92}$$

$$3C + 3O \rightarrow 3CO \uparrow \tag{93}$$

The details of this important industry will be found in Part 4.

225 Properties of Aluminum

Aluminum is a grayish-white, light metal possessing, for its weight, remarkable tensile strength which is increased greatly by the addition of small amounts of beryllium. It is very malleable and is therefore capable of being stamped into a great variety of forms without cracking. It is not easily dissolved by acids, though readily acted upon by alkalies, and it tarnishes superficially to the white oxide (Al_2O_3) alumina, which, being itself resistant to both acids and alkalies, protects the metallic surface from further attack. It is now enjoying wide use when alloyed with copper, magnesium, nickel and manganese. Next to iron, aluminum has become the most widely used metal.

The oxide Al_2O_3 is insoluble in water. If, however, the hydroxide $Al(OH)_3$ is precipitated by adding ammonium hydroxide to a solution of the chloride $AlCl_3$, it will form a colloidal solution of great absorptive capacity. This hydroxide is soluble in both acids and alkalies as follows:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O \tag{94}$$

Here it acts as a base, giving with hydrochloric acid the salt aluminum chloride and water:

$$Al(OH)_3 + 3NaOH \rightarrow Na_3AlO_3 + 3H_2O \qquad (95)$$

Here it acts as an acid, uniting with sodium hydroxide to give a salt, sodium aluminate and water. Thus it is both basic and acidic—a condition called *amphoteric*, that is, acting as both.

Aluminum metal is one of the constituents of thermite along with iron oxide. If this mixture is ignited, say, by magnesium ribbon, it will evolve great heat, producing molten iron and fumes of alumina (Al_2O_3). This is a useful method of welding iron rails, etc., the thermite mixture being packed around the ends and ignited. The reaction is

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \qquad (96)$$

The intense heat generated by the mixture has been used to melt ice jams where dynamite has failed. Thermite has also been used in incendiary bombs.

Aluminum oxide is much used as an abrasive for grinding parts of fine machinery, and aluminum chloride has a variety of applications ranging from cosmetics to the catalytic cracking of petroleum oils in the production of gasoline.

226 Group IV Non-metals and Metals

This group, like Group III, contains a number of elements (zirconium, hafnium, thorium and germanium) of lesser significance. Besides them are carbon, silicon and titanium in the IVA subgroup and tin and lead in IVB.

TABLE 19

Group IVA Non-metals

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Carbon	C	12.0	6	1.75 to 3.56	3527	....
Silicon	Si	28.1	14	2.0 to 2.50	1420	3500
Titanium	Ti	47.9	22	4.5	1800	5100

All these elements are tetravalent, forming such compounds as CO_2, SiO_2, TiO_2, H_2CO_3, H_2SiO_3 and H_2TiO_3. None of them forms cations in solution but all are acidic in their compounds.

Although simple compounds of carbon are soluble in water, most compounds of silicon and titanium are insoluble. Carbon has been separately treated in Chapter 7.

227 Silicon

Next to oxygen, silicon is the most abundant element in the earth's crust whether the atmosphere is included or not. This is shown in Table 20. It never occurs in a free state but always combined as silica (SiO_2) or the many silicates which, taken to-

TABLE 20

ELEMENTS IN THE LITHOSPHERE, THE HYDROSPHERE AND THE ATMOSPHERE

	1	2
Oxygen	49.42	46.71
Silicon	25.75	27.69
Aluminum	7.51	8.07
Iron	4.70	5.05
Calcium	3.39	3.65
Sodium	2.64	2.75
Potassium	2.40	2.58
Magnesium	1.94	2.08
Hydrogen	0.88	0.14
Titanium	0.58	0.62
Chlorine	0.188	0.045
Phosphorus	0.12	0.13
Carbon	0.087	0.094
Manganese	0.08	0.09
Sulfur	0.048	0.052
Barium	0.047	0.050
Chromium	0.033	0.035
Nitrogen	0.030	.....
Fluorine	0.027	0.029
Zirconium	0.023	0.025
Nickel	0.018	0.019
Strontium	0.017	0.018
Vanadium	0.016	0.016
Cerium, yttrium	0.014	0.014
Copper	0.010	0.010
Inclusive	0.032	0.033
	100.000	100.000

1. Average composition 10-mile crust, hydrosphere and atmosphere.
2. Average composition 10-mile crust, igneous rocks and sedimentary rocks.
Under "Inclusive" are listed all other elements.

gether, are the most abundant minerals in the earth's crust. Silicon is a gray-black, lustrous solid, hard and brittle. When finely divided it is brown and appears to be amorphous, whereas it is really crystalline.

The best-known compounds of silicon are its fluoride, carbide and oxide. The silicates are metallic salts of a great variety of acids, which are themselves impossible to prepare pure, for example, H_4SiO_4, H_2SiO_3, $H_6Si_2O_7$, $H_4Si_3O_8$.

Silicon tetrafluoride combines with hydrofluoric acid to form fluo-silicic acid:

$$SiF_4 + 2HF \rightarrow H_2SiF_6 \tag{97}$$

It also hydrolyzes in water to give a dense fog of silica particles:

$$SiF_4 + 2H_2O \rightarrow SiO_2 + 4HF \tag{98}$$

It has consequently been used as a smoke screen over water in naval operations.

Silicon may be prepared by reduction of silica with carbon in the electric furnace.

By fusing silica and coke in the electric furnace, silicon carbide (SiC) is produced. It is an extremely hard solid used as an abrasive of great industrial value, and sold under a number of well-known trade names.

A very pure form of silica is quartz, a hard crystalline material which, when colored by traces of impurities of iron and manganese, is known as amethyst, agate, onyx, etc., the semi-precious gem stones. On being fused at about 1700°C it can be molded into a variety of transparent, translucent forms, much in demand for the making of apparatus for chemical and optical use, since it is very resistant to chemical reagents (except hydrofluoric acid) and admits more ultraviolet light than does ordinary glass.

228 Group IVB Metals

TABLE 21

GROUP IVB METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Germanium	Ge	72.6	32	5.36	958	2700
Tin	Sn	118.7	50	7.31	232	2270
Lead	Pb	207.2	82	11.35	327.5	1620

Of the three metals shown here, germanium is very uncommon; its physical properties show a strong resemblance to beryllium in relation to the rest of the group.

Tin and lead are well-known elements with a great variety of industrial uses. Both are fairly resistant to corrosion, brittle and soft. Tin is divalent and tetravalent, for example, SnO, SnO_2, $SnCl_2$, $SnCl_4$; but tetravalence is the more stable condition. It is amphoteric as these examples show:

$$Sn + 2HCl \rightarrow H_2\uparrow + SnCl_2 \text{ (stannous chloride)} \tag{99}$$

$$Sn + 2NaOH \rightarrow H_2\uparrow + Na_2SnO_2 \text{ (sodium stannite)} \tag{100}$$

229 Tin

Tin is prepared by the reduction of its commonest ore, cassiterite (SnO_2), by means of coal or charcoal in a blast furnace. It was to obtain this oxide that the Phoenicians traded with ancient Britain, since the supplies obtained from Cornwall went into the manufacture of bronze when alloyed with the copper of Cyprus. The chief use of tin is in alloys and as a coating for thin sheet iron—tinned iron. Its resistance to attack by chemical agents, except to form a thin white protective coating of oxide, and the non-toxic nature of its compounds favor its use wherever food containers are made. Tin compounds likewise are useful to fix dyes in fabrics.

Malaya is the world's largest supplier of tin, with Bolivia second.

230 Lead

Lead occurs chiefly as the sulfide (galena, PbS) along with many important impurities such as zinc, copper, cadmium, arsenic, antimony, bismuth, silver and gold.

Lead is a soft, bluish-white metal, tarnishing easily in air and being dissolved by most acids except sulfuric. When softened by heat it can be fashioned into a variety of forms. It displays no allotropy and forms compounds in which it is mainly divalent, though sometimes tetravalent. Its compounds are definitely toxic, and in many countries the use of lead in making pottery has been discontinued for that reason.

Lead is obtained by reduction from its oxide using carbon and, because of its low melting point, is a constituent of many low-melting alloys. Its use is chiefly confined to the manufacture of those materials which require low tensile strength, such as pipes

in plumbing fixtures (the Latin *plumbum* means lead), and storage batteries.

The most important compound of lead is the so-called white lead [$Pb_3(OH)_2(CO_3)_2$] which has such great covering power (technically known as body) that it is universally employed in the manufacture of paints. It is a strange compound (if such it be) and has been used as a white pigment, and as a base for other pigments, for at least thirty centuries. Curiously enough the method of manufacture of the finest quality for this purpose has scarcely changed in all that time. Another lead compound which has come to the fore relatively recently is lead tetraethyl [$Pb(C_2H_5)_4$], a volatile addend to gasoline designed to prevent knocking, which is premature ignition in internal combustion engines. Like all lead compounds it is highly toxic, all the more so because of its volatility.

The many oxides of lead, PbO, PbO_2, Pb_2O_3, Pb_3O_4, have various industrial uses. Lead chromate ($PbCrO_4$) is a common yellow pigment.

231 Group VA Metals

The elements shown in Table 22 are relatively rare and are valued chiefly for their physical properties.

TABLE 22

GROUP VA METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.*, °*C*	*B. Pt.*, °*C*
Vanadium	V	50.95	23	5.87	1715	3000
Columbium	Cb	92.91	41	8.4	1950	>3300
Tantalum	Ta	180.88	73	16.6	2850	6110

These elements are steel-gray in appearance and are very hard. Vanadium is used for strengthening steel, columbium renders chromium weldable and tantalum is used to replace platinum wire in light bulbs. In addition to its high melting and boiling points, tantalum has a very low coefficient of thermal expansion, ranking with tungsten, molybdenum and iridium. Their use in special steel alloys is due to their physical properties. Vanadium pentoxide (V_2O_5) is replacing platinum as the catalyst in the Contact process for manufacturing sulfuric acid.

232 Group VB Elements

Of the two subgroups here, VB contains the majority of the elements and the best known.

TABLE 23

Group VB Elements

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt., °C*	*B. Pt., °C*
Nitrogen	N	14.0	7	Gas	−209.9	−195.8
Phosphorus	P	30.98	15	1.83	44	287
Arsenic	As	74.9	33	5.73	850	Sublimes
Antimony	Sb	121.8	51	6.7	630	1440
Bismuth	Bi	209.0	83	9.8	271	1450

Nitrogen has already been fully treated in Chapter 5.

Phosphorus is a non-metal, arsenic and antimony are metalloids and bismuth is a metal—an interesting transition going down the column. All five elements form many oxides and at least one hydride; for example, ammonia NH_3, phosphine PH_3, arsine AsH_3, stibine SbH_3, bismuthine BiH_3. All these hydrides are toxic, ammonia being the least so. Though nitrogen has three acids in all, phosphorus has eight, arsenic six, antimony two and bismuth none—further evidence that acid formation belongs chiefly to the non-metals.

233 Phosphorus

This element never exists free in nature because of its vigorous reaction with oxygen, but is found in such natural deposits as phosphorite, $Ca_3(PO_4)_2$ and apatite, $Ca_3(PO_4)_2 \cdot CaF_2$. Its preparation consists of heating, in the electric furnace, a mixture of phosphate, silica and carbon:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 10CO \uparrow + 6CaSiO_3 + P_4 \uparrow \quad (101)$$

The phosphorus distills off with the carbon monoxide, is condensed and is then run into appropriate containers. When so prepared it is a white waxlike solid which must be kept from exposure to oxygen, the halogens, etc., with which it unites with great vigor to form phosphorus pentoxide, etc.:

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \quad (102)$$

In insufficient oxygen it forms the trioxide:

$$P_4 + 3O_2 \rightarrow 2P_2O_3 \tag{103}$$

These two oxides are the anhydrides of six important acids.

When freshly prepared, the element is a soft, yellowish-white non-metal, which in the light slowly changes to a red powder. This change may be hastened by heating, the resulting product differing vastly from the white variety. Actually the allotropy of phosphorus is displayed by three principal modifications—the white, the red and a black crystalline solid produced by heating, under pressure, the white variety. The first and second modifications are the most interesting since their properties differ so widely. The white is soft and waxlike, melts at 44°C, is soluble in carbon disulfide, ignites spontaneously in the atmosphere to form oxides and on contact with human tissues develops a disease known as "phossy jaw." The red variety, on the other hand, is a powder which melts at about 500°C, is insoluble in carbon disulfide, does not ignite spontaneously in air or oxygen and is non-poisonous. On distilling red phosphorus, white vapors are evolved, which condense to form the white modification.

The principal use of the element is in the making of matches. Formerly the white variety was used in making matches, but this type of match was discarded because of phosphorus poisoning. Modern matches are of two types, the "strike anywhere" and the safety match. The first has a head tipped with a mixture containing a non-toxic sulfide of phosphorus (P_4S_3), the main portion of the head containing inflammable material similar to sulfur, together with some oxidizing agent such as potassium chlorate, all bound to the match by glue. The safety match has antimony sulfide (Sb_2S_3) in the tip with, say, potassium chlorate, powdered glass and glue. This tip, scratched upon a surface coated with red phosphorus, produces the flame. To prevent complete burning, the rest of the match is impregnated with ammonium phosphate.

234 Some Phosphorus Compounds

The various forms of phosphorus produce, of course, the same chemical compounds. Analogous to NH_3 is the poisonous gas phosphine, PH_3; with the halogens, phosphorus gives PCl_3, PBr_3, PI_3, the trichloride, tribromide and tri-iodide, respectively. On uniting with oxygen, two oxides may be produced—P_2O_3, the

trioxide, and P_2O_5, the pentoxide; the latter is a white solid much used as a dehydrating agent. These oxides dissolve in water to form acids: (H_3PO_3), phosphorous acid, (H_3PO_4), phosphoric acid, respectively.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3 \tag{104}$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \tag{105}$$

Of these two, the more important is the phosphoric acid because it gives rise to the phosphates. The three hydrogen atoms may be replaced separately by sodium to give: (1) sodium dihydrogen phosphate (NaH_2PO_4), which gives an acidic reaction; (2) the neutral disodium hydrogen phosphate (Na_2HPO_4); and (3) the alkaline trisodium phosphate (Na_3PO_4). All these salts are of importance in the human body.

From apatite by the action of sulfuric acid it is possible to prepare a soluble salt, calcium monophosphate [$CaH_4(PO_4)_2$], which, mixed with calcium sulfate ($CaSO_4$), is known as *superphosphate*. It is much used as a fertilizer in preference to the less soluble, crushed apatite.

Phosphorus is of importance to the growth of plants and is a necessary constituent of the animal body, not only of the bony structures but also of the cells, particularly those of the brain and nervous system.

235 Arsenic

Arsenic is found in combination with many metals along with their sulfides. When such ores are roasted, arsenious oxide (As_2O_3) is volatilized and passes off along with sulfur dioxide. When these mixed gases are cooled, the arsenious oxide solidifies to a white powder. Though resembling a metal in appearance, arsenic is definitely a non-metal, as it does not form a nitrate, sulfate or phosphate, though it forms a chloride ($AsCl_3$) just as does phosphorus (PCl_3). Such compounds indicate that arsenic is distinctly non-metallic, and this is supported by the acids which resemble the acids of phosphorus—the *-ous* and *-ic* types having the formulae H_3AsO_3, $H_4AS_2O_5$, $HAsO_2$, and H_3AsO_4, $H_4As_2O_7$, $HAsO_3$. Though these acids are unstable and tend to decompose to As_2O_3 and As_2O_5, respectively, the sodium and potassium salts are known. Arsenic is a metalloid and its hydroxides are amphoteric, leaning heavily towards the acid side.

Arsenic is alloyed with lead, brass, etc., and acts as a hardening agent. Its commonest oxide, As_2O_3 (usually called white arsenic), is used as a poison for rodents, and its compounds with lead and copper (for instance, Paris green) are important as pest exterminators on farms. Though dilute solutions of arsenic compounds are used medicinally as tonics, all such compounds are definitely toxic. This toxicity is of such importance in medical jurisprudence that the detection of arsenic in, say, stomach contents demands great accuracy. The test employed depends on the reduction of arsenic compounds by zinc and an acid, where the arsine produced is led off into a heated glass tube; here, if present, it deposits a film of metallic arsenic. This is a very sensitive test, detecting one ten-thousandth of a gram of the metal, and calling for use of reagents containing no arsenic themselves so as to insure accuracy. The conviction of many a person suspected of murder has depended on this test. The body of a victim of arsenic poisoning is bound, after death, to contain sufficient of the metal to react positively to this test, though cremation of the body causes disappearance of the arsenic through volatilization as the oxide.

236 Antimony and Bismuth

Antimony and bismuth occur naturally as sulfides. Both have the physical properties of metals, though antimony is more non-metallic in that it forms many acidic compounds. Both metals expand when solidifying (resembling water) and hence are of value in alloys with cadmium, copper, lead and tin. Some of these alloys have low melting points, which make them of importance in the manufacture of fuses for electrical wiring and sprinkler systems. A tartrate of antimony is used medicinally as tartar emetic, and bismuth compounds such as the basic carbonate [$Bi(OH)CO_3$] are much used in the preparation of antacids for the treatment of excessive acidity in the alimentary tract. Approximately three quarters of the world's supply of bismuth is used medicinally.

237 Group VIA Metals

Of these four elements the first three are by far the best known, the last being relatively rare and of interest chiefly because it is radioactive. These are hard metals, fairly resistant to corrosion and of importance in steel alloys. This is especially true of tungsten whose use in high-speed steels is largely dependent on its being

the metal with the highest melting point. Because tungsten is rarer than molybdenum, the latter is used wherever possible instead. These metals and others will be found treated at length in Chapter 18.

TABLE 24

GROUP VIA METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Chromium	Cr	52.01	24	7.1	1550	2482
Molybdenum	Mo	95.95	42	10.2	2680	4800
Tungsten	W	183.92	74	19.3	3372	5930
Uranium	U	238.07	92	18.7	>1850	....

These metals are amphoteric. When acting as the cation they are mainly trivalent, and when they form part of the anion they are, like sulfur, hexavalent. The following tabulation emphasizes this:

TYPES OF CHIEF COMPOUNDS OF CHROMIUM

Chromic sulfate $Cr_2(SO_4)_3$ blue	Potassium chromate K_2CrO_4 yellow
Chromic oxide Cr_2O_3 green	Chromic trioxide CrO_3 red

Potassium dichromate
$K_2Cr_2O_7$
red

Molybdenum and tungsten form similar compounds, all colored. These metals may be prepared by reduction from their oxides by aluminum or by carbon in the electric furnace.

238 Group VIB Non-metals

The two most important elements of this group, oxygen and sulfur, have already been discussed in Chapters 2 and 11. Selenium and Tellurium were named after the moon and the earth, respectively. Both are non-metals, dark in color and fairly hard. Their hydrides, hydrogen selenide (H_2Se) and hydrogen telluride (H_2Te) are gases, toxic and with disagreeable odors; their oxides and acids resemble those of sulfur. Selenium finds application in

the manufacture of ruby glass and because of its great sensitivity to light has been used in photoelectric cells. This sensitivity is accompanied by a great change in electrical conduction—hence the use of selenium to measure light intensities and for control of lights

TABLE 25

GROUP VIB NON-METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.*, °*C*	*B. Pt.*, °*C*
Oxygen	O	16	8	Gas	−218.7	−183
Sulfur	S	32	16	1.95–2.07	113–119	444
Selenium	Se	79	34	4.26–4.8	217	452
Tellurium	Te	127.6	52	6.01–6.27	452	1390

used in navigation and for a great variety of similar purposes.

Tellurium is used to toughen rubber, particularly in hose and cable coverings.

239 Group VIIA Metals

Two elements of this group are known, manganese and rhenium, and a third, masurium, has been identified in X-ray spectra. Manganese is the only one of importance. Its symbol is Mn, its atomic weight 54.93, atomic number 25, specific gravity 7.2, melting point 1240°C and its boiling point 2160°C.

Its only real similarity to the halogens is that Mn_2O_7 and Cl_2O_7 are both yellowish, highly explosive liquids. It shows its greatest resemblance to chromium whose compounds are of the same type except for valence. Following are the formulae of some of its compounds: MnO, Mn_2O_3, MnO_2, Mn_2O_7, $MnSO_4$, $KMnO_4$. The valences shown here are chiefly 2 (cation) and 7 (in the anion). Manganous sulfide, MnS, is pink as are all manganese salts, whereas potassium permanganate is a deep purple.

Manganese occurs chiefly as pyrolusite, which is largely manganese dioxide (MnO_2), itself of great commercial importance. Metallic manganese is prepared from this oxide by reduction and finds its major use as an alloy of iron. Potassium permanganate is used as an oxidizing agent. In dilute solution it evolves nascent oxygen and thus is used in quantitative analysis. It has also a limited use medicinally as a germicide and in the treatment for poison ivy infection.

240 Group VIIB—the Halogens

They have been treated previously in Chapter 9.

241 Group VIII—the Transition Group

TABLE 26

GROUP VIII METALS

Name	*Symbol*	*At. Wt.*	*At. No.*	*Sp. Gr.*	*M. Pt.,* °*C*	*B. Pt.,* °*C*
Iron	Fe	55.85	26	7.86	1536	3000
Cobalt	Co	58.94	27	8.9	1480	2900
Nickel	Ni	58.69	28	8.9	1452	2900
Ruthenium	Ru	101.7	44	12.2	2450	4150
Rhodium	Rh	102.91	45	12.5	1985	>2500
Palladium	Pd	106.7	46	11.4	1555	3980
Osmium	Os	190.2	76	22.5	2700	5500
Iridium	Ir	193.1	77	22.4	2440	4900
Platinum	Pt	195.23	78	21.45	1770	3907

The nine metals in this group show no coherent similarities as a whole, although three triads are found among them.

The first triad is iron, cobalt and nickel; the most common member is iron. All three metals are of medium hardness, and their physical properties show a close relationship to their atomic weight and number as Table 26 indicates. None occurs free in nature. Iron is found as oxide, carbonate and sulfide chiefly; cobalt occurs in combination with arsenic and sulfur; and nickel in association with sulfur along with iron, cobalt and copper. All are obtained from their ores by roasting and subsequent reduction (see Chapter 32).

Iron, unless specially alloyed, is rapidly oxidized to an oxide ("rusting"). This deterioration may be prevented or delayed by coating with a metal such as tin or zinc. Iron is readily attacked by acids, forming two types of salts, namely, ferrous, in which it is divalent as in the sulfate ($FeSO_4$), and ferric as in the chloride and sulfate [$FeCl_3$ and $Fe_2(SO_4)_3$]. Of these two types, the ferric is the more stable. In fact, ferrous salts on exposure to oxygen tend to become ferric. Ferrous salts are usually a pale green, and the ferric compounds a pale to deep red-brown.

242 Cobalt and Nickel

These are interesting metals resembling iron chemically in many ways, though much less subject to corrosion. Their chief use is in

plating and alloying with other metals. The importance of nickel lies in the strength and flexibility it imparts to its alloys. For that reason it is in great demand in the manufacture of all types of machinery subject to hard usage, for example, in the sheathing of battleships and the working parts of heavy engines. Canada is the chief producer of nickel.

Of the other metals in this group, platinum (Pt) is the most important chemically because of its resistance to all ordinary reagents except aqua regia, which is a mixture of two strong acids, nitric and hydrochloric, in concentrated solution. Platinum is also slowly attacked by fused alkalies and free chlorine. Although worth only a few cents an ounce (Troy) a hundred years ago, the demand has grown steadily. In 1918 it commanded the unusual price of $125 an ounce because of the great demand for catalytic usage in war industries and the collapse of the Russian army, Russia being at that time almost the sole producer of platinum. The demand for other sources of supply led to the discovery of the valuable deposits in Canada, which is now the second producer of platinum and allied metals in the world; Colombia and South Africa are third and fourth.

Platinum occurs native but never pure, being associated with other metals of the same group; for example, Canadian sources show a ratio of 1 part of palladium to 1.4 parts of platinum. It is obtained chiefly as a by-product in the refining of nickel-copper ores. Palladium in a fine state of subdivision (palladium black) is an excellent catalyst, being capable of absorbing many times its own volume of hydrogen. Iridium, another element of the same group and occurring along with platinum, is very hard and is alloyed with platinum in small quantities in jewelry and in fountain pen nibs.

An interesting physical property of platinum is that it is ductile to an enormous extent, one ounce (Troy) of the pure metal being able to produce a wire over 10,000 miles long and not more than one hundred-thousandth of an inch in diameter. Sixty per cent of all platinum is used in the manufacture of jewelry, 9 per cent in chemical industry and 16 per cent in dentistry.

243 Summary

Out of several attempts to correlate the properties of the elements has arisen the formulation due mainly to Mendelejeff—the periodic classification of the elements, called briefly the periodic table (page 197).

This arrangement is built on the successive increase in atomic weight (and atomic number) from hydrogen onwards. It results in the formation of vertical families or groups of elements (sometimes subdivided). These groups and subgroups show a great similarity among the individual members in valence and in properties both physical and chemical.

Groups I to VII show in their numerals (1) the number of valence electrons and (2) the valence to oxygen of the atoms in their respective groups.

Hydrogen possesses a unique atomic structure and is not included in any group.

The first member of each group is rather more different from the other members than the latter are among themselves. The members of a sub-group for example, Cu, Ag, Au, tend to resemble the members of the next group rather more than they do the members of the main group to which they belong.

Group 0 contains the inactive, rare gases, Group IA the most active metals. This metallic, electropositive activity merges as we traverse a series, into the amphoteric and metalloid elements to end up in Group VII with the non-metallic, electronegative, reactive halogens.

Group VIII, called the "transition group" contains nine metals with a wide variation in physical and chemical properties; they do not fit into any group hitherto mentioned. They have to be considered individually rather than as a single group.

Questions

1. Trace the attempts to classify the elements.
2. Write down the first two horizontal lines of Mendelejeff's table and comment on (*a*) their atomic weights and (*b*) their valence.
3. Define and exemplify the terms: amphoteric, allotropic, metalloid.
4. Review the elements listed in this chapter and classify them as to: (*a*) their uses in medicine; (*b*) their variation in valence; (*c*) the toxicity of their compounds; (*d*) their occurrence in North and South America.
5. Why is zero the appropriate group number for the rare gases?
6. Draw a sketch to show electronically the formula of magnesium chloride.
7. "The element phosphorus is both life-sustaining and death-dealing." Comment on this statement.
8. What do the following terms mean to you: Döbereiner; periodic; nucleus; series; mono-; inert; alkali; aqua regia; electroplating; limelight; amalgam?

18

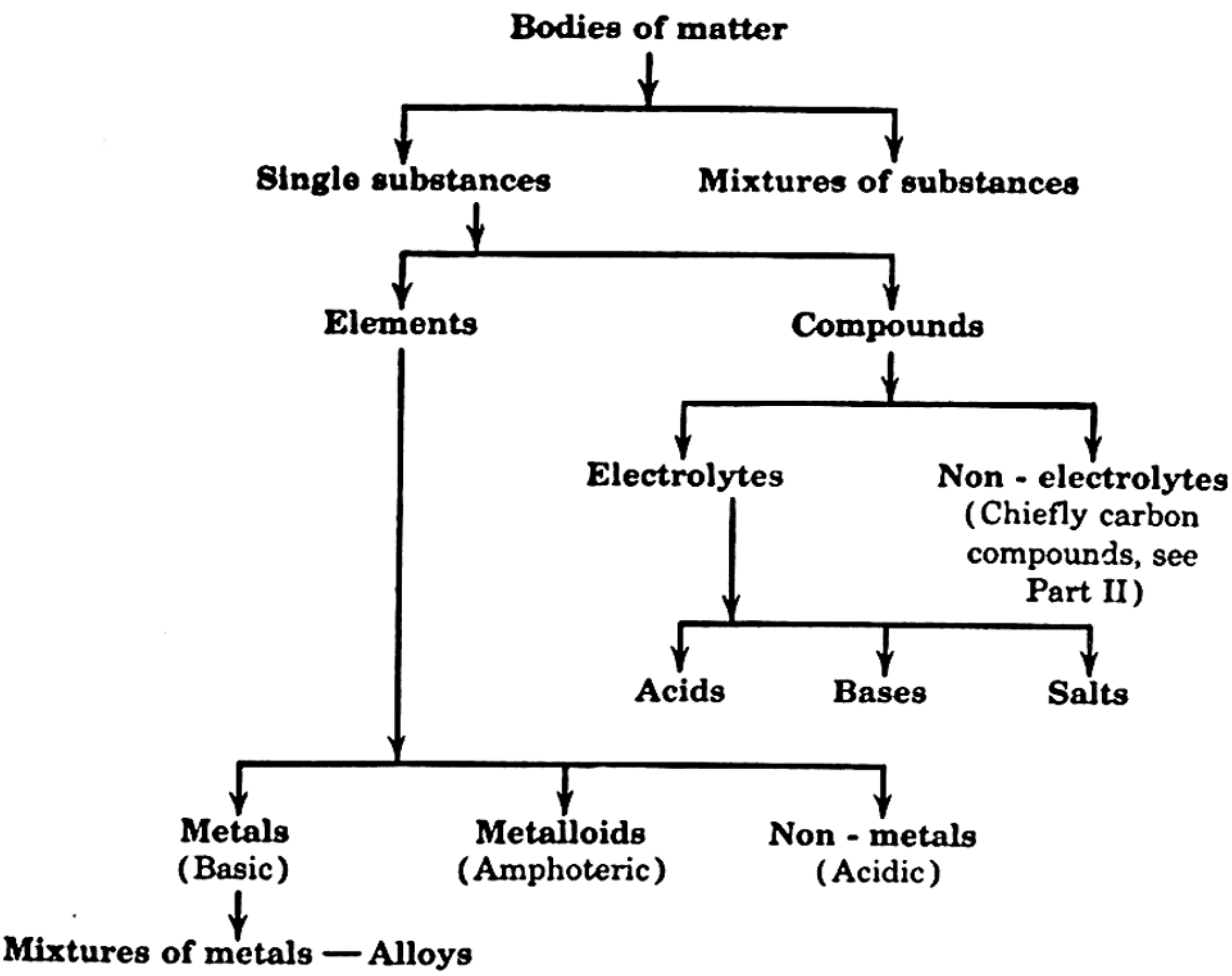
Metals—Alloys

244 Classifications

In the preceding chapters we have used various methods of classifying the kinds of matter we have studied. Table 27 summarizes them.

TABLE 27

Classification of Chemical Bodies



Except for a few isolated examples, such as diamonds and particles of gold, all matter with which we come in contact is com-

posed of a mixture of substances and chiefly of a mixture of chemical compounds rather than of elements. These mixtures of substances are separated by the chemist into the individual substances, which are later resolved into elements and compounds.

Compounds are divisible into electrolytes, which constitute the chief study of inorganic chemistry, and non-electrolytes. This latter class, by far the more numerous, is concerned mainly with carbon compounds to be treated in Part 2 of this book. Such compounds are held together by covalence chiefly, that is, by a sharing of electrons.

Electrolytes, on the other hand, show the phenomenon of electrical conduction in solution and demonstrate the existence of electrovalence, that is, a giving up and receiving of electrons so that ions and radicals may have an individual existence distinct from that of the atom. The division of electrolytes into acids, bases and salts draws attention to the differences in chemical reaction (for instance, neutralization) among these three.

The elements arrange themselves according to their atomic number into the groups shown in Chapter 17. The elements in Group 0 show no chemical behavior because of a completeness in their electronic arrangement. But the very active metals in Group IA are the antithesis of the very active non-metals in Group VIIB. The atoms of the former release their lone external electron with great ease to have it taken up by halogen atoms to produce ions whose electronic structures take on the arrangement of the nearest rare gas. This electron-giving ability of, say, sodium is greater than that of magnesium and still greater than that of aluminum. In Group IV this ability has almost disappeared to be replaced by electron receiving, which reaches its climax in chlorine in the same series of the Periodic Table. This transition from electron release to electron reception passes through a region in the middle of the Periodic Table which shows amphoterism; aluminum, tin and chromium are good examples of this property. In this same region are the metalloids, whose physical and chemical properties, as demonstrated in the Periodic Table, resemble the metals and non-metals.

To attempt to define metals and non-metals with relation to their physical properties only is extremely difficult, as may be seen from the following. The diamond is harder than either chromium or tungsten; color varies too much to be of assistance

here; sulfur has a greater specific gravity than sodium, but both are below platinum, gold or copper; all metals are good electrical conductors, but so is graphite; arsenic, a metalloid, has the luster of a metal and a high specific gravity, but does not form a cation.

But any element which at ordinary temperatures is a gas may be labeled a non-metal. Any element (except hydrogen) which gives rise to a cation in solution is almost without exception metallic. A metal may, when associated with a non-metal (as AlO_3), form an anion, whereupon the metal may show amphoteric properties and then belongs to the class of metalloids.

An element which in solution gives rise to an anion is a non-metal, for example, Cl^-, I^-, $S^=$. When such an element is associated with another non-metal in the ionic state, the ion is always an anion, for example, ClO_3^-, $SO_4^=$.

A *metalloid* thus becomes an element which shows the luster and electrical conductivity so common among metals but the chemical reactions of a non-metal. Arsenic and antimony in Group V are the best examples of the above definition, and vanadium, chromium, molybdenum, tungsten, tin, lead and aluminum in the same region of the Periodic Table qualify to varying degrees for the same distinction.

Table 28 shows some comparative values for the physical properties of the best-known metals.

Those elements which we can safely call metals, as well as some which are metalloids, assume much greater importance in our industrial life than the non-metals. At first glance it would seem that the non-metals hydrogen, oxygen, nitrogen, sulfur and phosphorus are of major importance in the world because of their concern with the existence and well-being of plants and animals. By contrast, the metals might appear to be of lesser value to the vital economy. If it means anything it certainly is true that our modern civilization has grown upon the ever-increasing production and use of metals and metalloids; hence the tendency to emphasize their importance. Their value to modern life lies chiefly in their physical properties and in how these may be modified. A single example will suffice to explain this. Iron, pure iron, is not very hard and is liable to rapid corrosion in the atmosphere and in chemical reagents. Industrially it cannot be said to be of any use. When alloyed, however, first with carbon, which when present, even to the extent of 0.2 per cent, changes its physical properties

TABLE 28

SOME PROPERTIES OF THE METALS

Metal	Sp. Gr. at 20°C	M. Pt., °C	B. Pt., °C	Hardness	Electrical Conductivity (Reciprocal Ohms)	Tensile Strength (lb/in.^{2})	Heat Conductivity
Aluminium	2.70	660	1800	2	324,000	30,000–40,000	0.48
Antimony	6.7	630	1440	3	27,100		0.04
Beryllium	1.85	1282	2780	6–7	54,100		
Bismuth	9.8	271	1450	2.5	9,260		0.019
Cadmium	8.65	321	778	2.0	146,000		0.222
Calcium	1.55	810	1488	1.5	95,000		
Chromium	7.1	1550	2482	9.0			
Copper	8.92	1083	2310	2.5		60,000–70,000	0.918
Cobalt	8.90	1483	2900		83,200		
Gold	19.3	1063	2600	2.5	468,000	20,000	0.70
Iron	7.86	1536	3000	4	131,000	50,000	0.161
Lead	11.35	327.5	1620	1.5	50,400	2,600–3,300	0.083
Lithium	0.53	186	1336	0.6	119,000		
Magnesium	1.74	651	1110	2.0	230,000	33,000	0.376
Manganese	7.42	1240	2100				
Mercury	13.54	−38.9	357	Liquid	10,630		0.0148
Molybdenum	10.2	2680	4800				
Nickel	8.90	1452	2900		144,200	155,000	0.142
Palladium	12.16	1555	3980	4.8	97,900		
Platinum	21.45	1770	3907	4.3	91,200	50,000	0.1664
Potassium	0.86	62	760	0.5	150,500		
Silver	10.5	960	1950	2.5	681,200	42,000	0.974
Sodium	0.97	97	880	0.4	211,000		
Tantalum	16.6	2850	6110	. . .	60,600		
Tin	7.31	232	2270	1.5	76,600	4000–5000	0.155
Tungsten	19.3	3372	5930			590,000	0.35
Zinc	7.14	419.5	907	2.5	186,000	22,000–30,000	0.265

extraordinarily, and later with various quantities of vanadium, manganese, chromium, molybdenum, tungsten and nickel, the resulting steels with their heat treatments raise iron to a place of first importance in world industry.

PHYSICAL PROPERTIES OF METALS

245 Melting Point

With only two exceptions all the metals and metalloids are solids at ordinary temperatures. Their melting points range from mercury −38.9°C through cesium 26°, lithium 186°, tin 232°, lead 327°, aluminum 659°, gold 1063°, iron 1536° to tungsten 3372°. By contrast, the non-metals show a melting point for helium of −272°C through phosphorus 44° and 725°, boron 2300° to carbon and silicon well above 3500°C. The range shown by the non-metals in melting point is therefore very great in comparison with metals. The melting point of a metal has great bearing first on the ease of production from its ores and second on its utilization in industry, particularly in the form of an alloy.

246 Boiling Point

The boiling point of a liquid is a measure of its vapor pressure even below its boiling point. The boiling points of the metals and metalloids vary from 357.3°C for mercury through cesium 673°, cadmium 770°, zinc 930°, magnesium 1110°, antimony 1440°, iron 3000°, tungsten 5930° to tantalum 6110°.

There is a general relationship between the hardness of a solid and its boiling point, and the above figures show it. Obviously the harder a metal and the higher the boiling point, the more its usefulness for high temperature operations.

The boiling points of non-metals are usually much lower than those of the metals and metalloids except carbon and silicon; sulfur, for example, a typical non-metal, boils at 445°C.

An interesting sidelight on the boiling and melting points of the metals is afforded by subtracting the latter from the former. This value, in degrees centigrade, is the range of temperature over which the substance exists as a liquid; a suitable name for this value is *liquid persistence*. It is interesting to note that values up to 797°C in liquid persistence include most of the alkali and alkaline earth metals, and values beyond 2100°C contain the Group VIII metals.

Other relationships can be found here which suggest that liquid persistence may be related to the nucleus of the atom rather than to the electronic structure.

247 Hardness

On the arbitrary scale of hardness where the diamond is given the value of 10, the values range from sodium 0.4 through silver 3, iridium 6 and beryllium 7 to chromium 9. By contrast sulfur is only 2.5. Obviously the gaseous non-metals have no hardness. Since the alkali metals are so soft that they can be cut very easily with a knife, and mercury is well known for its liquid state, the property of hardness will not distinguish metals from non-metals.

248 Ductility and Malleability

Ductility is the property which refers to the ability of a metal to be drawn into a wire without breaking; malleability expresses the degree to which a metal can be hammered into sheets. Gold is the most malleable and ductile of all the metals; it can be hammered to a thickness of one-two hundred and eighty thousandth of an inch and a gram of it drawn into a wire over 2 miles long. The following table shows the commoner metals arranged in de-

TABLE 29

SOME PROPERTIES OF THE COMMONER METALS

Ductility	*Malleability*	*Electrical Conductivity*	*Heat Conductivity*	*Tensile Strength*
Gold	Gold	Silver	Silver	Tungsten
Silver	Silver	Copper	Copper	Nickel
Platinum	Copper	Gold	Aluminum	Copper
Aluminum	Aluminum	Aluminum	Nickel	Platinum
Iron	Tin	Zinc	Iron	Silver
Nickel	Platinum	Iron	Platinum	Aluminum
Copper	Lead	Nickel	Tin	Magnesium
Zinc	Zinc	Lead	Gold	Gold
Tin	Iron	Mercury	Zinc	Iron
				Zinc
				Tin

creasing order of their ductility, electrical and heat conductivities and tensile strength of the pure, unalloyed metals.

249 Electromotive Series

In Table 11 on page 191 the metals are listed in decreasing order of their chemical activity. Thus potassium is more violent in its reaction with water at ordinary temperatures than sodium; magnesium requires a temperature of 100°C to give a similar reaction; and iron needs to be red-hot to form the oxide with water and liberate hydrogen. The metals below iron do not liberate hydrogen from water or steam at all readily. All the metals down to and including lead will liberate hydrogen from dilute acid solutions whereas those below will not do so. The oxides of the first six metals are not reduced by heating with hydrogen whereas those of iron to copper are, but the oxides of the last five are reduced merely by heating, as Priestley found when he heated HgO and discovered oxygen. The metallurgy of these metals shows that the first five may not be obtained from their ores by reduction with carbon. The occurrence of the ores of these metals shows a definite relationship to their position in this table.

The electrical relationships in Table 11 are emphasized by these statements:

(1) The elements at the top give up their electrons more readily than those farther down.
(2) If we take hydrogen as the standard of electron giving, this table can be arranged with assigned voltage values.
(3) A piece of zinc added to the aqueous solution of a copper salt will cause (*a*) the zinc to dissolve and (*b*) an equivalent quantity of copper to be deposited:

$$Zn + Cu^{++} + SO_4^{=} \rightarrow Zn^{++} + SO_4^{=} + Cu \downarrow \qquad (106)$$

(4) If two rods, say of copper and of zinc, are immersed in a solution of sulfuric acid, the zinc will dissolve to form ions, and a current will flow through a wire joining the bars of zinc and copper externally. It is on this voltage differential that (*a*) the precipitation of metals, (*b*) the operation of "wet" and "dry" batteries and (*c*) the generation of electricity by chemical means are based.

250 Alloys

Alloys are of two general kinds, ferrous and non-ferrous. Ferrous alloys are based on iron as the chief constituent, whereas the

non-ferrous may contain any metal except iron. Alloys may be regarded as solid solutions where one or more metals may be dissolved in another. This statement does not rule out the possibility of a compound between any pair of metals in the whole mass of alloy.

Alloys may also be classified according to the industrial use to which they may be put. For example, some alloys are required because their melting points are much lower than those of individual metals; others are in demand for such special properties as hardness, resistance to corrosion and tenacity.

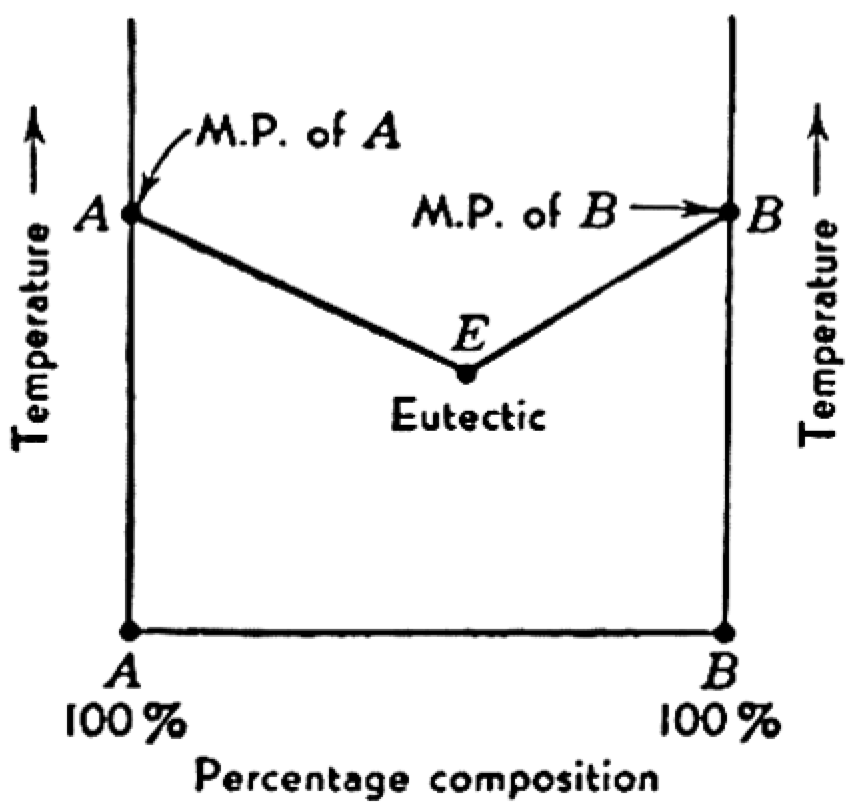


FIG. 64. Freezing (or melting) point curves of two substances soluble in each other.

Non-ferrous alloys may be used to illustrate the first classification given above. Alloys are usually prepared by melting the metals together in the proportions desired and allowing the mixture to cool. The simplest case can be treated as a sequel to the freezing point rule of Raoult. In Fig. 64 is plotted the concentration-freezing point curve for an ideal case. On the left we see the melting point of the pure substance A, which is soluble in all proportions in B. The melting point of B is given on the right, the temperature being plotted vertically. On the horizontal axis are plotted the percentage concentrations of A and B. The curve AE is obtained by dissolving increasing quantities of B in A; the curve BE is obtained by dissolving increasing quantities of A in B. According to the rule of Raoult, a solute lowers the freezing point of a solvent. Both these curves in a simple case meet at E; E, the lowest melting point mixture of A and B, is known as the *eutectic* point. As long as the melting points of A and B are not too far apart, E will in all simple cases be below the melting point of both components. Most cases are more complex than this one.

Here are a few examples of alloys based on the principles shown in Table 30.

Permalloy contains Fe 20 per cent and Ni 80 per cent and is very easily magnetized by feeble currents.

TABLE 30

Ferrous Alloys

Added Elements	*Uses*	*Properties Enhanced*
Mn	Machine tools	Toughness
Cr, V	Stainless steel, armor	Corrosion resisting
Ni	Armor plate	Tenacity
Si	"Duriron" tanks	Acid resisting
W, Mo, Co	High-speed tools	Temper retention at high temperatures

Nichrome (Ni, Cr, Fe, Mn) is used in electrical appliances as it withstands corrosion at high temperatures.

Stainless steel, for cutlery, contains Cr 12–15 per cent, C 0.2–4 per cent, Mn 0.2–0.45 per cent, Si 0.2–0.3 per cent.

Invar, Fe 64 per cent, Ni 36 per cent, has a very low coefficient of thermal expansion and is used for pendulums, etc.

TABLE 31

Non-ferrous Alloys

(Based on Group VIII metals)

Chromel, Ni 60 per cent, Cr 40 per cent
Manganin, Ni-Mn-Cu, standard resistance wires
Stellite, W-Co-Cr for high-speed tools
Palau, Pd-Au a substitute for platinum

TABLE 32

Non-ferrous Alloys (General)

Name	*Composition*	*Name*	*Composition*
Aluminum bronze	Cu, Al	Wood's metal	Bi, Cd, Sn, Pb
Babbitt metal	Cu, Sn, Sb	White metal	Cu, Sn, Pb
Bell metal	Cu, Sn	Rose's metal	Bi, Sn, Pb
Britannia metal	Cu, Sn, Sb	Shot	As, Pb
Brass	Cu, Zn	German silver	Cu, Zn, Ni
Duralumin	Cu, Al, Mg, Mn	Gun metal	Cu, Sn, Zn, Pb
Magnalium	Mg, Al	Nickel coin	Ni, Cu
Pewter	Sn, Sb	Silver coin	Ag, Cu
Solder	Sn, Pb	Gold coin	Au, Cu
Type metal	Sn, Pb, Sb		

251 Uses of the Metals

A few metals are sufficiently resistive to the action of the atmosphere to be used in the pure state. Among them are the noble metals, gold, platinum and silver, the last tarnishing slowly with the formation of the oxide or sulfide or both. Gold has the disadvantage of being very soft and so must be alloyed with some harder metal such as copper; pure silver is likewise too soft for much handling (as in coinage) and is similarly alloyed. Silver as used in coins is referred to as sterling, and is the 9 to 1 alloy with copper. Gold-copper alloys used in jewelry have their degree of fineness (gold content) expressed in carats; thus 14 carats fine means 14 twenty-fourths gold and 10 carats fine 10 twenty-fourths.[1]

Among the more common metals, tin and zinc are used as protective coatings for sheet iron, known as tinned iron and galvanized iron, respectively. Nickel, cadmium and chromium are frequently electroplated on to less resistive metals, chromium of late years having replaced nickel because of its bluish tint and more brilliant luster. Both gold and silver are used for electroplating, the latter because of its whiteness being much preferred over other metal finishes.

Copper and lead in sheets are very suitable for exterior work on buildings, the former oxidizing to a carbonate which has an artistic green color, making it much in demand for roofings, etc. Leaden drains wear well when coated with the black oxide, and the metal, because of its flexibility and low melting point (327°C), can be bent and molded into a great variety of forms, such as cylindrical casings for electrical wiring and plumbing connections.

Pure iron, on the other hand, is never used for such purposes as are mentioned above since it is too susceptible to weathering (rusting). Its alloys, however, with carbon, nickel, chromium, molybdenum, tungsten and vanadium—the ferrous alloys—are in great demand.

The demand for light, tough, but at the same time resistant, alloys has brought about the use of aluminum and magnesium, whose specific gravity is 2.7 and 1.72, respectively, as compared

[1] Here the word carat means a twenty-fourth part, and must not be confused with the carat which is a measure of weight for precious stones and is equal to 0.2 gram.

with 8.89 for copper. These metals alone, or with small proportions of other elements added, have great tensile strength.

Where alloys are required showing specially high resistance to corrosion from live steam, acids, etc., nickel and copper with small amounts of iron and manganese are found very suitable. Copper as a component of alloys displays its important properties of tensile strength and high electrical conductance, some copper alloys being preferable to steel. Bronze, for example, an alloy chiefly of copper and tin, is much harder than either and replaces steel in the making of castings where rusting would be objectionable.

Alloys containing two or more of the metals nickel, chromium, copper, manganese, zinc and iron show resistance to the passage of the electric current; thus they find application in the manufacture of such electrical equipment as standard resistances and heating elements in toasters, irons, etc.

Mercury is a useful solvent for some metals, particularly gold. Alloys of mercury and other metals are called *amalgams*. From them the mercury can easily be separated by boiling.

Of late years the researches carried on from the purely scientific point of view have disclosed the quite unpredictable changes in properties that follow the alloying of metals, with the discovery of materials that fit in with the rapidly changing demands of modern industry. Man's ingenuity and industry have carried him far in the development of alloys since the dubious metallic defences of Boadicea and Montezuma. Perhaps a concise summation of all the factors which contribute to power as it is now recognized, both nationally and internationally, would give a predominant place to alloys, since, without them, motion, the obvious sequel to power, would fall far short of what we have attained in the last half century.

252 Summary

Metals and non-metals are two divisions of the elements; those elements which partake of the properties of both divisions are called metalloids.

Metals enter into our industrial and domestic life to a greater extent than non-metals, and for this reason should have more consideration.

Both metals and non-metals possess many physical properties in common, but metals in general display luster, malleability and ductility not usual among the non-metals.

By chemical rather than by physical properties metals can be distinguished from non-metals. Metals produce bases or alkalies, whereas non-metals pro-

duce acids when united to hydrogen or oxygen or both. Most metals contract on solidification; exceptions are antimony and bismuth.

Metals form physical mixtures with one another. These mixtures are known as alloys, and in some instances they may partake of the nature of compounds.

Alloys of metals frequently show properties very different from the elements which enter into their composition, as exemplified by their melting points.

The importance of metals depends chiefly on their physical properties, such as hardness, ductility, malleability, heat and electrical conductivity, tensile strength and melting point. Their continued use depends on these properties and on their resistance to corrosion and abrasion, that is, on their chemical properties. In consequence, alloys represent an attempt to combine both physical and chemical properties.

Questions

(Both Chapters 17 and 18 are needed to answer these questions.)

1. Compare the hardness of diamond and steel, graphite and lead, aluminum and lampblack.
2. Compare the relative weights of aluminum and iron, charcoal and sulfur.
3. What differences can be found between the oxides of metals and those of non-metals?
4. What are alloys?
5. List all the different uses to which metals are put in your home.
6. The metals are an essential factor in industrial life. Can you show on a world map from what countries these metals are obtained?
7. A "strategic metal" is one of paramount importance in time of national crisis. Write an essay on the subject: "Is my country self-sufficient in strategic metals?"
8. What conclusions can you draw from a study of the "liquid persistence" of any eight metals?
9. Review the electromotive series of the metals and answer the following: (*a*) Name the two metals which should give the highest voltage when placed in a reacting liquid. Do you see any difficulties involved here? (*b*) What should happen when a strip of magnesium is dipped into aluminum chloride solution? (*c*) Would you construct a cell of silver and mercury?
10. How would you proceed to find how much of some metal can be deposited by 96,500 coulombs?
11. What do you understand by the terms (*a*) electromotive series and (*b*) electrochemical equivalent?
12. Compare aluminum and copper as to (*a*) their industrial uses and (*b*) their physical properties. What conclusion can you draw from your comparison?
13. For what special properties are (*a*) osmium, (*b*) iridium, (*c*) palladium noted?
14. How would you detect traces of arsenic in the stomach of a person alleged to have died of arsenic poisoning?
15. Why is hydrogen sulfide so useful in detecting metals in their salts?
16. What elements emit bright colors when heated?

Part 2

ORGANIC CHEMISTRY

19

Organic Chemistry—the First Steps

253 Historical Background

The term *organic* has been applied to a part of the study of carbon compounds to distinguish it from what has formed the main consideration in the preceding chapters—the inorganic. This was at first a more justifiable distinction than it is today. Organic chemistry, as it was first called in the early part of the nineteenth century, was essentially the study of chemical substances which resulted from the activities of living cells, such as starch, sugar, fats and proteins. In differentiating between inorganic and organic chemistry, it is apparent that, if organic chemistry is concerned only with the chemistry of the animate, inorganic chemistry should include only the inanimate world. To peer into the mysteries whose origin was so obviously divine was held to be outside the realm of science altogether. Indeed this belief was currently held, and a halo, as it were, enveloped the sanctity of life processes. It was undoubtedly this attitude—though not the attitude of the scientists—which led to the rise of carbon chemistry at a much later date than would otherwise have been inevitable.

True, dyes from plants and animals, perfumes from plants of many kinds and extracts from both kingdoms were in common use prior to the Christian era. But their chemical composition was neglected until Lavoisier isolated and analyzed some fifty of the commoner constituents of ordinary fruits. But the progress in botany, particularly from the physiological angle, naturally stressed the importance of chemical substances concerned in growth and reproduction. Lavoisier and others had stressed the universality of oxygen and carbon dioxide interchange in both plants and animals, but little was known of the chemistry of carbon compounds in 1800 by comparison with the large and well-correlated

knowledge of metals and their ores in the sixteenth century. It would seem that the scientific world awaited a sign. In any event, in 1826 Wöhler, by the simple process of heating, supplied it by his synthesis of urea, the compound excreted by such a large proportion of the animal kingdom, from the inanimate, inorganic compound ammonium cyanate (NH_4OCN). The last link in the chain of superstition had been broken, and the whole vista of carbon chemistry was opened up. But because of Wöhler's synthesis, perhaps, rather than in spite of it, carbon chemistry continued to be called organic.

254 Coming of Age

From the first the progress of organic chemistry was rapid—so rapid, indeed, that it had to invent its own names, its own theories and its own procedures. Synthetically it outstripped contemporary inorganic theory, developing its own theory of valence, for example, with its own picture of a carbon atom to account for such variations in the structure of compounds as had no counterpart in the older, staid inorganic branch. It thus became anything but organic, even going so far as to develop compounds in the laboratory to replace those which had been collected from the life cycle of plants for generations.

But the twentieth century has seen a return to the organic idea in the rise of an offshoot of this carbon chemistry. This is the child of chemistry and of physiology, and it has grown rapidly as biological, or physiological, chemistry or, for short, biochemistry—the chemistry of living cells. It is the true organic chemistry, but successful chemists in this field must have also an accurate knowledge of inorganic chemistry and its theoretical offshoot, the so-called physical chemistry. The chemistry of the carbon compounds is the title preferred by most chemists for this science, since it raises no issue about origins.

Hitherto the formulae given have been represented chiefly in the empirical manner, HCl, H_2SO_4, Na_3PO_4, etc. It will be found necessary from now on, for reasons which will appear in due course, to represent carbon compounds by graphical formulae.

255 Linking the Atoms

Unlike inorganic compounds, the various combinations based on carbon are very susceptible to such atomic arrangement as may

be regarded as a sort of jigsaw puzzle. The different parts composing this puzzle are few, and the rules are simple. It is thus possible to compose aggregations which are as simple or as complex as we wish to make them. Indeed, it was formerly customary to consider atoms as spheres, each of which possessed a number of hooks on which other atoms having hooks could hang. Our present method of representing such compounds differs very little from this old one. True, we discard the spheres, but we retain the hooks as connecting rods, or bonds as we call them. These bonds bind the atoms together to form compounds, the only restriction in their use being that the number of bonds emanating from any atom must accord with the valence of that element whose atom we are considering.

256 The Tetrahedron

In actual practice we go so far as to represent these compounds, as indeed they must exist, in space, in three dimensions. Under these circumstances the carbon atom is represented as a regular tetrahedron (Fig. 65), that is, a four-sided, four-edged, four-pointed solid figure, whose angles, sides and edges are separately equal. A set of such figures would help later in elucidating certain structural difficulties, but for the present we can get along very well in our two-dimensional circumstances, that is, by writing on the flat surface of paper or blackboard.

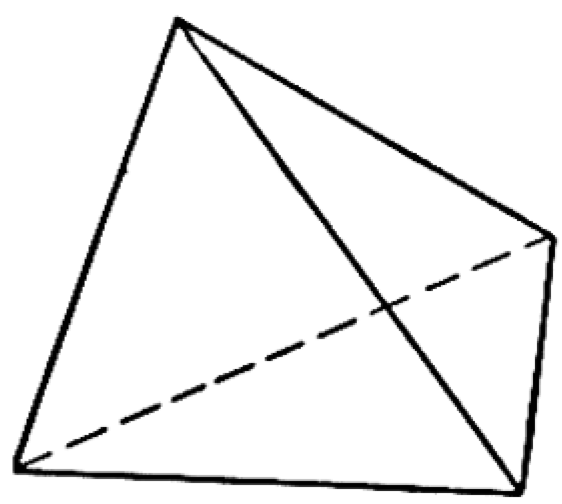


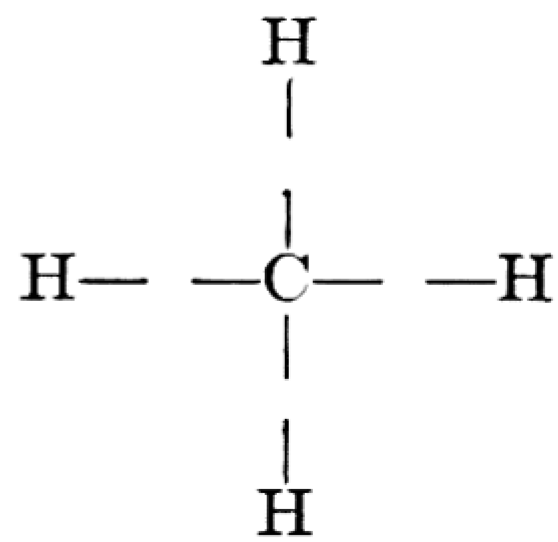
FIG. 65. A regular tetrahedron.

The pieces of our puzzle so far are: carbon, with a regular valence of 4 (as in CO_2), which may be represented by $-\overset{|}{\underset{|}{C}}-$; hydrogen, our standard of valence, represented by H—; chlorine, by Cl—; and oxygen, by —O— or O═.

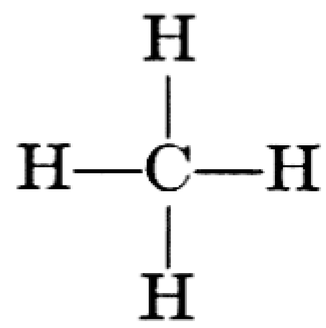
257 A Hydrocarbon

We are now ready for picture making. We take the carbon atom with its four bonds and fill up these bonds with other elements so as to have no bonds left over anywhere. For one carbon atom with its four bonds we see at once that we can use four hydrogens that will answer our specifications. Set down the carbon atom with its

four bonds, and place the hydrogen atoms so that their bonds correspond with those of the carbon atom.

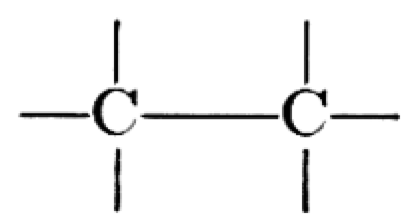


Now join the bonds as you see them and the picture is

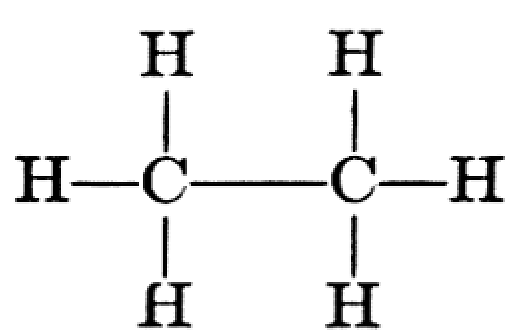


This is the simple carbon compound, made up of carbon and hydrogen only, and of only one carbon atom at that and the fewest hydrogen atoms possible so as to leave no unjoined bonds. This is a hydrocarbon, called methane.

Suppose that we start with two carbon atoms and join them. We get this picture



one valence bond of each of the two carbon atoms being taken up with joining these atoms. There are thus six free bonds left over. On each of these bonds a hydrogen can be placed, giving us



This is another compound made up of carbon and hydrogen only—therefore it is a hydrocarbon, and its name happens to be ethane.

So we can go on; but since these are pictorial representations of our two compounds, we call them *graphical* formulae, as compared with the grouped formulae CH_4 and C_2H_6, which are called

empirical formulae. It may be recalled that H_2SO_4 represents a compound with certain properties both physical and chemical. However, this formula does not tell how, for example, the oxygen atoms are joined within the molecule.

In organic compounds it makes all the difference in the world, not so much what atoms are joined, as how they are joined. This important *how* is understood only by visualizing the picture of the atoms linked together.

258 Introducing Chlorine

But we have used only carbon and hydrogen so far. Looking back we see that chlorine (also bromine and iodine) is represented as having one bond. So we can find room for four chlorine atoms on one carbon atom thus:

```
     Cl
     |
Cl—C—Cl
     |
     Cl
```

This is a liquid commonly called carbon tetrachloride, and it is used as a solvent for fatty substances and as a fire extinguisher.

Now let us take one carbon atom and mix in the picture both hydrogen and chlorine. Since in valence hydrogen and chlorine atoms are equal and carbon has room for four altogether, we can have the following pictures:

```
    H            H            Cl
    |            |            |
H—C—Cl       H—C—Cl       H—C—Cl
    |            |            |
    H            Cl           Cl
```

Notice that we have been increasing the chlorine and decreasing the hydrogen in the formulae as we wrote them down from left to right. The first of them, in which we have one chlorine atom in place of one of the hydrogen atoms in methane, is methyl chloride, a gas commonly used in small household electrical refrigerators because it is less objectionable in case of breakage than either ammonia or sulfur dioxide. The second is methylene chloride. The third is the liquid anesthetic, chloroform. The same sort of

replacement of hydrogen by a halogen would give, in the case of iodine, the compound

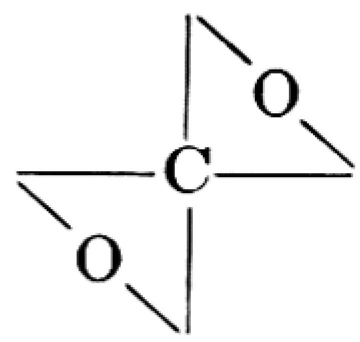
$$\begin{array}{ccc} & I & \\ & | & \\ H— & C & —I \\ & | & \\ & I & \end{array}$$

which is called iodoform, a well-known disinfectant.

Of course we can write all these compounds in the empirical manner, for example, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4 and CHI_3. In these examples it would really make no difference, but in a little while we shall find examples which oblige us to use the graphical forms only.

259 And Then Oxygen

If we begin to use oxygen in these pictures we must remember that the oxygen atom is divalent and has two bonds. However, if we use carbon and oxygen only,

$\begin{array}{c} | \\ —C— \\ | \end{array}$ and —O—, we can easily make  ,

or, more simply, O═C═O. This is our old carbon dioxide (CO_2) and the picture is correct, for on the four bonds of carbon we can hang two oxygen atoms, each of which has two connecting bonds to represent divalence.

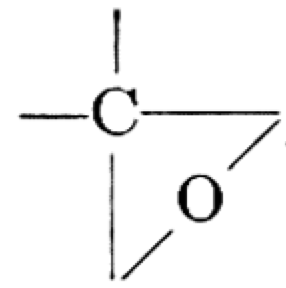
260 An Alcohol

If, again, we use both hydrogen and oxygen with our carbon atom, we can make further pictures. We can, for example, put together one carbon and one oxygen thus: $\begin{array}{c} | \\ —C—O— \\ | \end{array}$ but this leaves four bonds free to hold something. Let us put a hydrogen on each bond and we get

$$\begin{array}{ccc} & H & \\ & | & \\ H— & C & —O—H \\ & | & \\ & H & \end{array}$$

This picture is now correct according to the rules, and we have here the graphical formula of methyl (or wood) alcohol.

261 An Aldehyde

If we had put the carbon and oxygen together thus , or better —C=O, we should have had only two free bonds to which to attach hydrogens. This would give us H—C(H)=O, which is the formula for formaldehyde, a gas used largely as a disinfecting agent.

262 Is All This Real?

We can go on indefinitely making such pictures, but at about this stage the student of classical inorganic chemistry has a suspicion of unreality. This suspicion arises mainly from two facts: first, that in inorganic chemistry we feel obliged to prepare something in some way or other and then to discuss its properties; and, second, that we must be dealing with something that is very easily explained, since there are many facts in inorganic chemistry of which we know the how but not the why. Actually the reply to this hypothetical criticism is that we are dealing with a very few pieces in our puzzle, not with the eighty-odd elements other than carbon, hydrogen, oxygen and the halogens, and that these pieces do not show variable valence, such as silver, gold, mercury, sulfur do. But the fundamental reason back of all this is that students of carbon chemistry about seventy years ago evolved a conception of valence which simply had to work in order to explain such apparent differences when compared with inorganic compounds. In addition, we have dozens of compounds all belonging to the same family and therefore being prepared similarly, having very similar physical and chemical properties. But for inorganic compounds there are so many variations that if a graphical system were helpful it would have been evolved a century ago.

Just as for other compounds, carbon compounds had to be isolated and analyzed, their molecular weights found and their chemical properties ascertained before any speculation as to the

inner arrangement of their atoms could be made. It has been done so well and so thoroughly that we now have an intimate record of over a hundred thousand compounds.

263 A Few Descriptions

In order to give reality to the compounds we have stuck together on paper, we shall study them from the practical point of view for a few pages. But it should nevertheless be clearly understood that any compound we can put together on paper in conformity with some half dozen simple rules can actually be made in the laboratory, so much so that nowadays most of the discoveries are made first on paper and then turned over to practical chemical manipulators for realization.

264 Methane

Methane (CH_4) is a gas found in oil wells and also produced when certain complex carbon compounds are strongly heated. It burns in air or oxygen to give carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (107)$$

It does not react with such reagents as hydrochloric, nitric and sulfuric acids and sodium hydroxide, but reacts readily with chlorine and bromine. When the latter reaction occurs, a molecule of chlorine (Cl_2) reacts with a molecule of methane to give two products—a molecule of hydrogen chloride and a compound answering to the formula CH_3Cl. This may best be represented graphically:

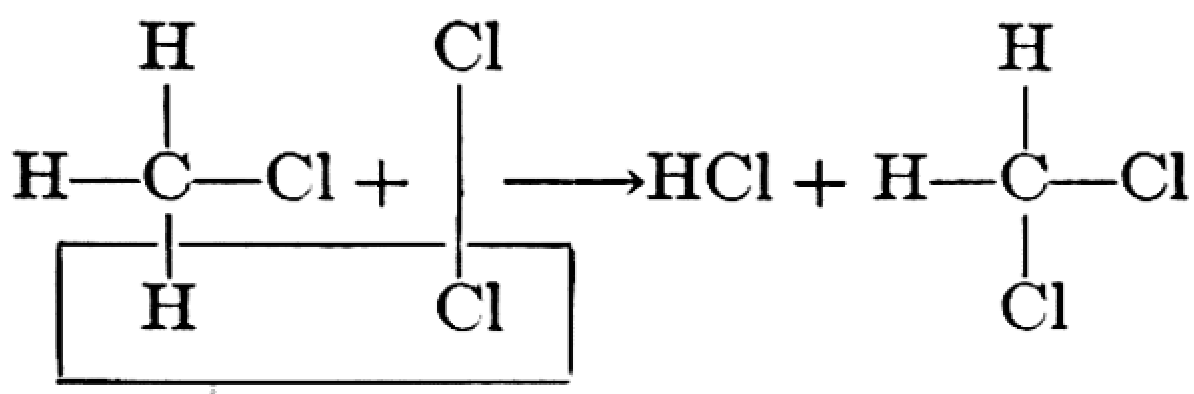
$$\underset{\text{Methane}}{\begin{array}{c}\mathrm{H}\\ | \\ \mathrm{H—C—}\\ | \\ \mathrm{H}\end{array}}\underset{\text{Chlorine}}{\boxed{\mathrm{—H + Cl—}}\mathrm{—Cl}} \longrightarrow \underset{\text{Hydrogen chloride}}{\mathrm{HCl}} + \underset{\text{Methyl chloride}}{\begin{array}{c}\mathrm{H}\\ | \\ \mathrm{H—C—Cl}\\ | \\ \mathrm{H}\end{array}} \qquad (108)$$

265 Substitution by a Halogen

In this equation we see that the chlorine molecule has split, one atom taking away from the CH_4 a hydrogen atom to form hydrogen chloride and the other atom going in to fill the vacancy left. This replacement of one hydrogen by one chlorine atom, known as *substitution*, is an important type of reaction and quite

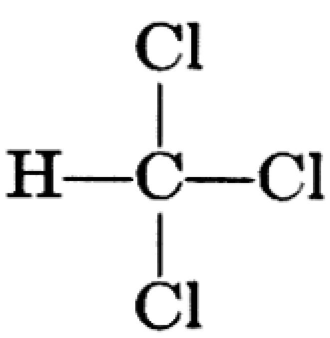
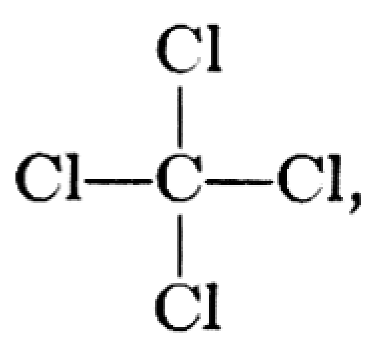
common to hydrocarbons. The product of this reaction, CH_3Cl, methyl chloride, is also called (mono) chloromethane (chloro + methane).

The substitution illustrated above will, in the case of methane, continue further thus:



(109)

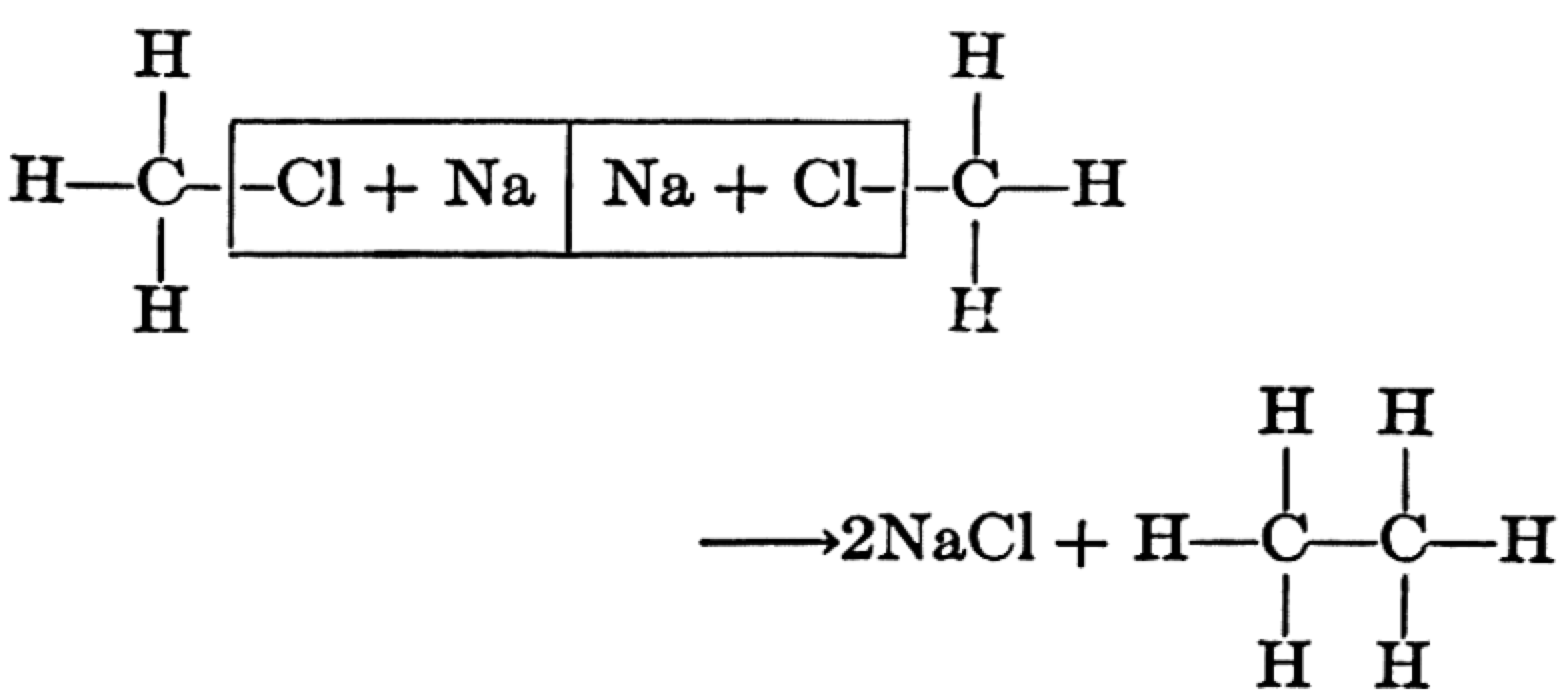
Methyl chloride (or chloromethane) — Chlorine — Hydrogen chloride — Methylene chloride (or dichloromethane)

Similarly  and , respectively chloroform [or trichloromethane (tri + chloro + methane)][1] and carbon tetrachloride [or tetrachloromethane (tetra + chloro + methane)], will be obtained if sufficient chlorine is used.

266 Synthesizing a Hydrocarbon

There are two interesting reactions of methyl chloride which are appropriate here.

1. When treated suitably with metallic sodium, sodium chloride is split off and ethane is synthesized, thus

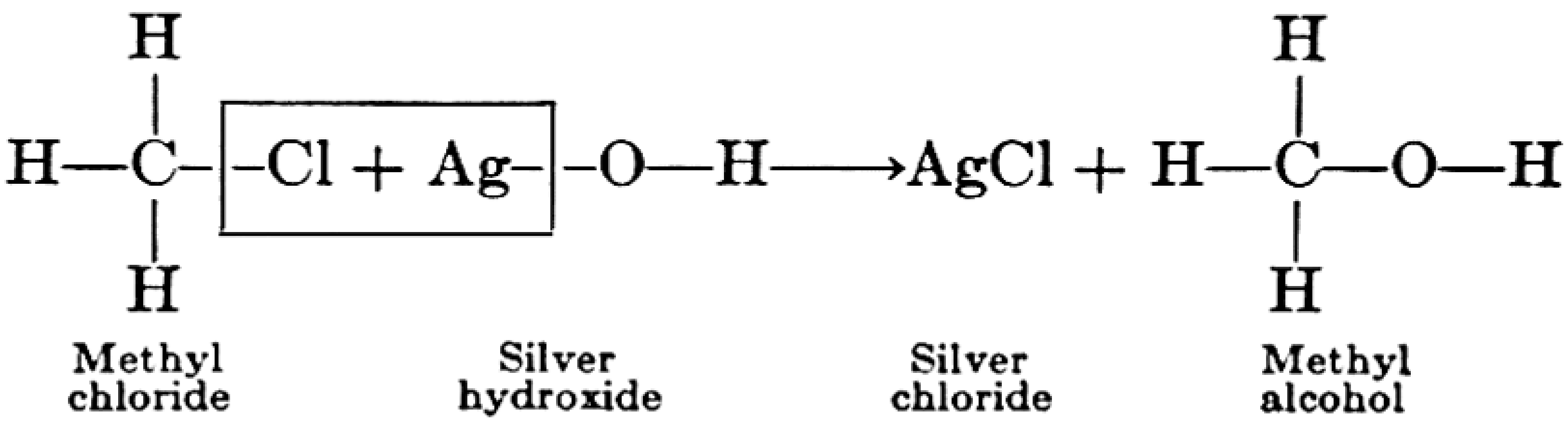


(110)

[1] The names in brackets are newer than the others given and are part of a system of nomenclature which places the name of the parent hydrocarbon last, and indicates by mono, di, tri, etc., how many times the halogen atom (in this case chlorine) has substituted for one hydrogen in that hydrocarbon.

We have synthesized a hydrocarbon from a *lower* one, that is, from one with fewer carbon atoms.

2. When treated with an inorganic hydroxide, such as silver hydroxide (AgOH), the metal removes the chlorine, whose place is taken by the monovalent radical —OH. Thus



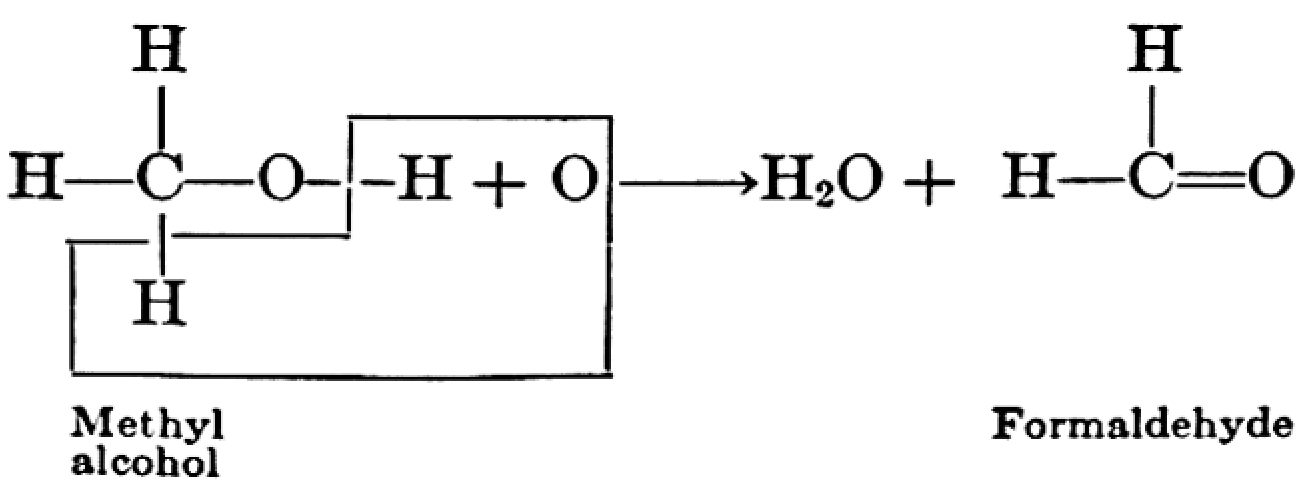
(111)

267 Methyl Alcohol

The compound CH_3OH, one having the linkage —C—O—H, is known as an alcohol. The prefix methyl, derived from methane, means CH_4 minus one hydrogen; CH_3 cannot exist long alone but may be found linked to many other atoms, that is, it is a radical. Methyl alcohol is a colorless, inflammable liquid, boiling at 65°C and much used as a solvent. It may also be obtained commercially by heating wood out of contact with air.

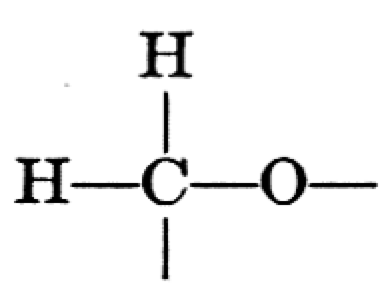
268 Formaldehyde

Alcohols are easily oxidized by means of simple oxidizing agents. The oxidation here means the removal of hydrogen. Thus



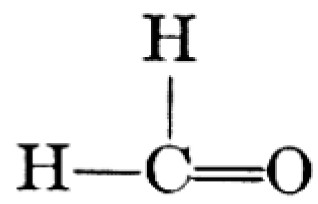
(112)

The removal of two atoms of hydrogen from CH_3OH (one being that attached to O) apparently leaves the carbon and oxygen with unattached bonds thus

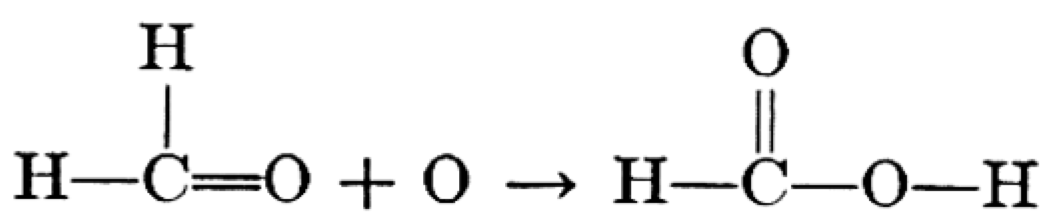


But this is a stable compound and possesses properties which would

indicate that the oxygen is linked entirely to the carbon. Hence we write it



that is, with what is called a *double bond* between the oxygen and the carbon, and we refer to the oxygen found in aldehydes as *doubly bound* oxygen. This compound HCHO is not named from methane but from its oxidation product (see below). Formaldehyde is a gas, commonly dissolved in water and methyl alcohol under the name of formalin. When this gas is oxidized it picks up an atom of oxygen thus

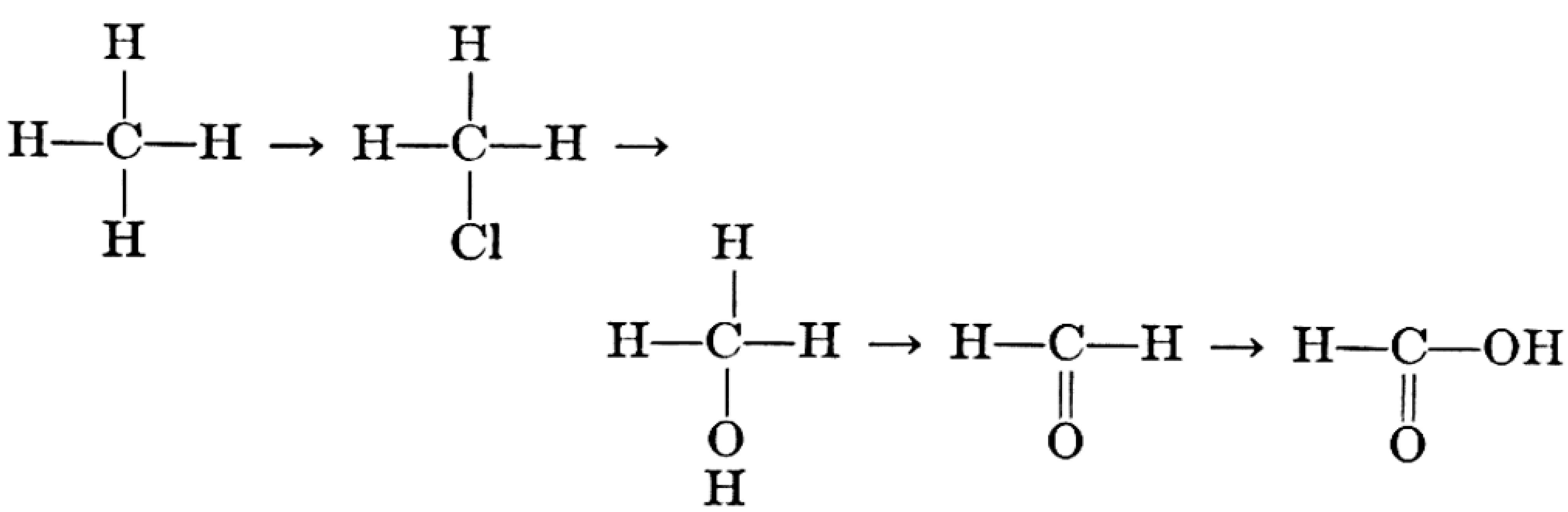


Formaldehyde Formic acid (113)

The result of this oxidation is the formation of —OH attached to the carbon in place of one hydrogen of the formaldehyde. Formic acid, the product, is an acidic liquid boiling at about 100°C. It was first prepared by distilling red ants; hence the name (Latin, *formica* = ant).

269 Graphical Review

The main feature of this chapter is the stress laid on the interrelationship of the compounds treated. It may be represented conveniently in the following manner:



This portrays the chemical transition from a hydrocarbon to a halogenated hydrocarbon, thence to an alcohol, an aldehyde and, finally, to an acid. There is a great deal of chemistry represented here, and this chart will be found of value later.

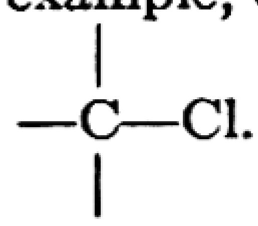
270 Summary

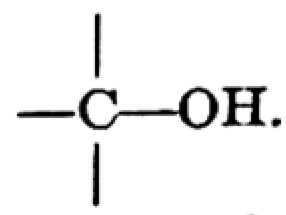
The chemistry of carbon and its many compounds was originally called organic chemistry because it was connected with the products of life. The subject is so large now that it includes in the main a multitude of compounds not known to be synthesized in nature.

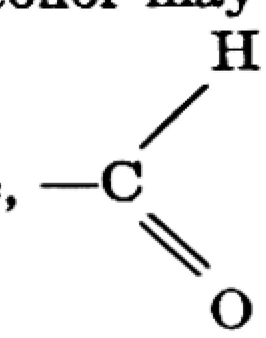
Carbon chemistry lends itself to systematic study for several reasons. First, there are few elements, and they have simple valences—carbon 4, oxygen 2, hydrogen and the halogens 1, nitrogen 3 to 5, etc. Furthermore, all known compounds can be assigned to some family, whose members may be many but whose reactions are similar.

Graphical formulae, imperative in carbon chemistry, consist mainly of chains of carbon atoms of valence 4 and capable of holding a variety of radicals.

The simplest family of carbon compounds is the paraffin hydrocarbons—methane, ethane, etc., which are composed of carbon and hydrogen only.

These hydrocarbons react only with halogens, for example, chlorine, by substitution. A halogenated hydrocarbon is produced, .

Replacing one such halogen by OH gives rise to an alcohol, .

An alcohol may suffer oxidation (losing two hydrogen atoms) to give an aldehyde, 

An aldehyde may be oxidized to form an acid, —COOH.

Hydrocarbons, alcohols, aldehydes and acids are well-known families whose members act in concert. Their actions are determined by what radical (for example, —OH, —CHO, —COOH, etc.) they possess. Such radicals are called *functional groups*.

It therefore really makes a difference how the atoms are joined together in a carbon compound—not so much what individual atoms or how many of each are present.

The importance of graphical formulae is that they permit us to see at a glance to what family a compound belongs and consequently how that compound will act chemically.

Questions

1. Outline the rise of organic chemistry.
2. Using bonds to represent valence, draw diagrams to illustrate a hydrocarbon, carbon dioxide, an alcohol and an aldehyde.
3. Show diagrammatically how one may prepare formic acid from methane.

20

Pictures from the Paraffins

271 Looking Backward

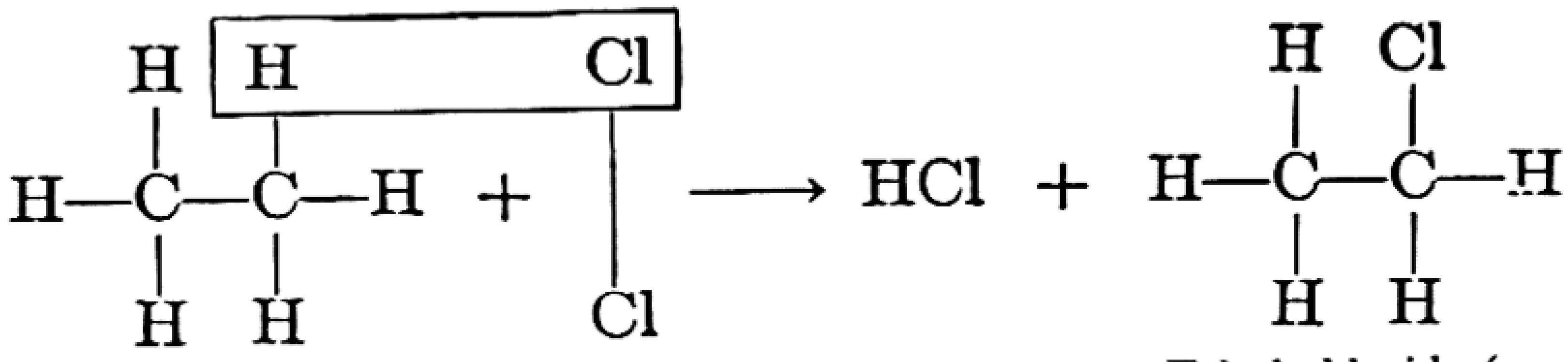
We are now ready to group together these compounds we have actually prepared. This is best accomplished in a progressive manner as indicated in the following chart. For convenience we shall use condensed graphical formulae, omitting some of the bonds but retaining the structure where essential:

$$\begin{array}{ccccccccc}
\text{Hydro-carbon} & & \text{Cl derivative} & & \text{Alcohol} & & \text{Aldehyde} & & \text{Acid} \\
CH_4 & \rightarrow & CH_3\text{—}Cl & \rightarrow & CH_3\text{—}OH & \rightarrow & H\text{—}CHO & \rightarrow & H\text{—}COOH \\
 & \swarrow & & & & & & & \\
\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} & & & & & & & &
\end{array}$$

The top line represents the individual compounds spoken of previously. They are also the simplest members of the families of hydrocarbons, chlorine derivatives of these hydrocarbons, alcohols, aldehydes and acids. Consideration of the above pictures will permit us to draw up a few definitions. A hydrocarbon is a compound of carbon and hydrogen only. An alcohol is a compound having an —OH group attached to a carbon atom without any other oxygen on that carbon atom. An aldehyde is a compound having the radical $-\underset{\underset{\displaystyle H}{|}}{C}=O$ (or shortly —CHO) attached somewhere. An acid is a compound having the radical $-\underset{\underset{\displaystyle O}{\|}}{C}-O-H$ (or shortly —COOH) attached somewhere.

272 The Second Hydrocarbon

The simple chart above contains also ethane, a second hydrocarbon. Let us now treat this with chlorine just as we did methane:



Ethane — Chlorine — Hydrogen chloride — Ethyl chloride (or monochloroethane, mono + chloro + ethane) (114)

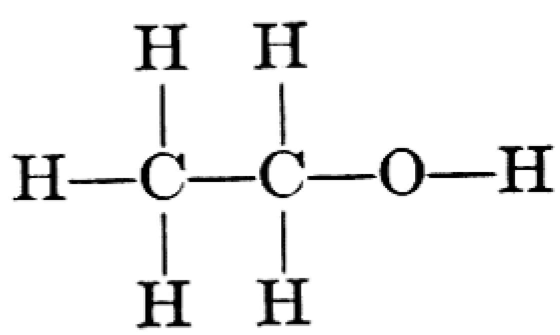
We may for convenience shorten the last formula to $CH_3 \cdot CH_2Cl$ or C_2H_5Cl. This last formula shows how the name ethyl chloride is obtained.

273 Ethyl Alcohol

Now treating this chloride, as we did methyl chloride, with an inorganic hydroxide we obtain ethyl alcohol:

$$CH_3CH_2\boxed{Cl + Ag}OH \longrightarrow AgCl + CH_3CH_2{-}OH \qquad (115)$$

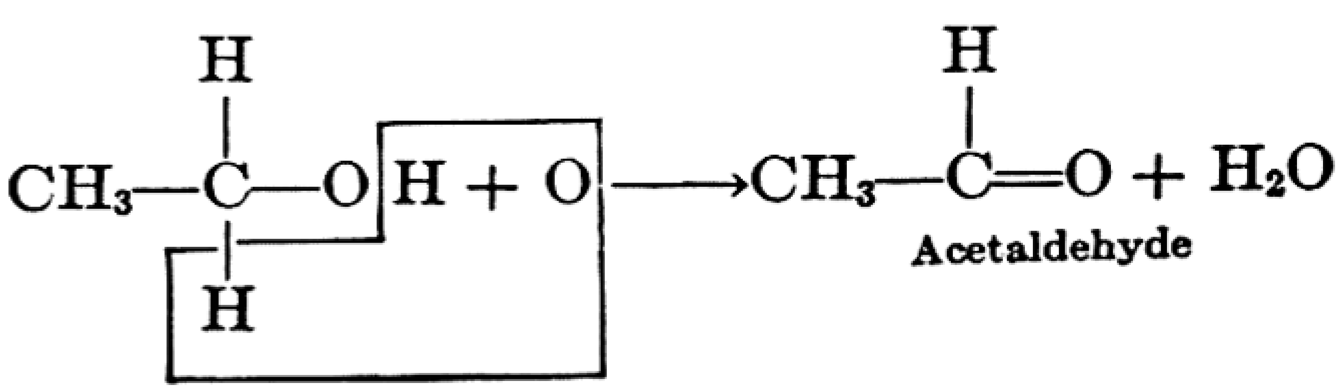
This when spread out fully is



According to definition, this is another alcohol. As a matter of fact it is the alcohol which, because it is used in beer, wines and liquors, is commonly referred to as just alcohol. It may be prepared by fermentation.

274 Acetaldehyde

Now let us oxidize this alcohol as we did methyl alcohol:



Acetaldehyde (116)

It is written more shortly as $CH_3 \cdot CHO$ and takes is name from its oxidation product as follows:

$$CH_3 \cdot CHO + O \rightarrow \underset{\text{Acetic acid}}{CH_3COOH} \qquad (117)$$

275 Acetic Acid

Acetic acid is found in vinegar to the extent of 6 to 8 per cent. Vinegar is prepared for human consumption by allowing alcohol-containing liquids (such as light wines) to ferment. Acetic acid, when pure, is a crystalline solid at 16°C and a colorless liquid at higher temperatures. It boils at a temperature somewhat above the boiling point of water and, though an acid, is not a strong one.

276 Graphical Review

We now have an additional line for our chart (§ 271), and together the two lines are:

$$\begin{array}{ccccccccc}
\text{Hydro-carbon} & & \text{Chlorine derivative} & & \text{Alcohol} & & \text{Aldehyde} & & \text{Acid} \\
CH_4 & \rightarrow & CH_3Cl & \rightarrow & CH_3OH & \rightarrow & HCHO & \rightarrow & HCOOH \\
\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} & \rightarrow & \begin{matrix} CH_3 \\ | \\ CH_2Cl \end{matrix} & \rightarrow & \begin{matrix} CH_3 \\ | \\ CH_2OH \end{matrix} & \rightarrow & \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} & \rightarrow & \begin{matrix} CH_3 \\ | \\ COOH \end{matrix}
\end{array}$$

In considering the second line in conjunction with the first, using contracted graphical formulae and omitting the reagents or methods of preparation, we shall be struck by certain regularities. Each compound of the second line falls into one of the previous families; and, also, the compounds in any one vertically arranged family differ from each other by one carbon and two hydrogen atoms, that is, CH_2. If, then, we were to add CH_2 to each compound of the second line, we should get compounds as follows: $CH_3 \cdot CH_2 \cdot CH_3$, $CH_3 \cdot CH_2 \cdot CH_2Cl$, $CH_3 \cdot CH_2 \cdot CH_2OH$, $CH_3 \cdot CH_2 \cdot CHO$, $CH_3 \cdot CH_2 \cdot COOH$. These formulae are of compounds that really exist and in this relationship. They would form a third line, and their names are propane, propyl chloride (or monochloropropane, mono + chloro + propane), propyl alcohol, propionic aldehyde and propionic acid.

277 Homologues

Thus we have five families of carbon compounds and three representatives of each. There are more such representatives—

many more than we need worry over. But when we find a series of compounds, all belonging to the same family, where the members, when written down in order of increasing number of carbon atoms, show a constant difference of CH_2, we call such a series *homologous*, and each member a *homologue* of the others.

278 Paraffins

Incidentally, there are many families of hydrocarbons. But methane, ethane and propane have such formulae as show no carbon atom joined to another carbon atom by more than one bond; hence they are called saturated hydrocarbons. Also, all these hydrocarbons (up to C_{60}) are not easily attacked by chemicals other than chlorine and bromine; hence they are called the *paraffin* hydrocarbons (paraffin = little affinity).

279 Going Backward

In our scheme we have seen how an acid may be prepared in steps from the parent paraffin hydrocarbon. It enables us to show the structural relationships existing among these compounds and provides us with methods of preparation. In the same two senses a reverse transformation from right to left in our scheme would be useful. Thus if the acid is formed into the sodium salt and heated with sodium formate, the aldehyde is obtained from the acid (unless that acid is formic). Also, as aldehydes are formed from alcohols by oxidation, so alcohols may be prepared from their corresponding aldehydes by reduction. Again if alcohols are treated with phosphorus trichloride, the —OH is replaced by —Cl, thus forming the halogenated hydrocarbon.

Last, this halogen derivative suitably treated (with magnesium powder and later with water) gives back the corresponding[1] hydrocarbon. (See chart on page 249.)

We now have five classes or families of organic compounds, and each such family has many members. Only a few of the members will engage our attention later. Meanwhile, from the families shown there are several new ones obtainable, as outlined in the following paragraphs.

[1] The word *corresponding* is used throughout to mean possessing the same number of carbon atoms, irrespective of what other atoms may be found in the compounds.

280 An Ether

A mixture of an alcohol and a dehydrating agent (such as concentrated sulfuric acid) when warmed gives off a gas which may be condensed to a colorless liquid of low boiling point. Analysis of its composition and structure points to its being an oxide, which bears the same relation to an alcohol as sodium oxide (Na_2O) does to sodium hydroxide (NaOH).

$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}O}\\ |\\ \mathrm{H}\end{array}\boxed{\begin{array}{l}\mathrm{H + HO}\\ \mathrm{H_2SO_4}\end{array}}\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{{-}C{-}H}\\ |\\ \mathrm{H}\end{array}\longrightarrow\begin{array}{c}\mathrm{H}\quad\ \mathrm{H}\\ |\qquad |\\ \mathrm{H{-}C{-}O{-}C{-}H}\\ |\qquad |\\ \mathrm{H}\quad\ \mathrm{H}\end{array} + \mathrm{H_2SO_4\cdot H_2O} \tag{118}$$

The sulfuric acid acts only to extract one molecule of water from the atoms of two molecules of the methyl alcohol. The resulting compound [written shortly as $CH_3{-}O{-}CH_3$ or $(CH_3)_2O$] may be called dimethyl oxide, but is more usually referred to as dimethyl ether. It is the simplest ether of all.

281 Diethyl Ether

Similarly ethyl alcohol treated in the same way yields diethyl ether, written as $CH_3\cdot CH_2{-}O{-}CH_2\cdot CH_3$ or $(C_2H_5)_2O$. It is the ether which is usually called just *ether*, on account of its common use as an anesthetic. As it is made on a large scale with sulfuric acid and ethyl alcohol, it is technically known as *sulfuric ether*.

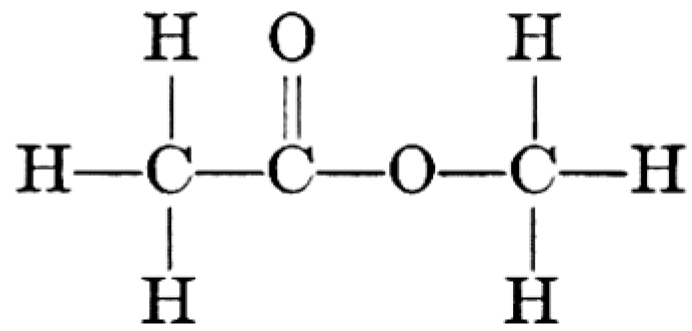
282 An Ester

If sodium hydroxide is treated with hydrochloric acid, a salt and water are formed. Similarly, although the analogy is not a perfect one, an alcohol and an acid will form water and a compound made up of organic parts:

$$\underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Acetic acid}}{CH_3\cdot COOH} \rightarrow H_2O + \underset{\text{Methyl acetate}}{CH_3\cdot COO\cdot CH_3} \tag{119}$$

This "organic salt" was formerly called an ethereal salt because it could be so easily transformed into a gas. Later it was called an *ester*, whose specific name is that of the alcohol and acid from which it is made. It will be observed that the conventional way of writing

the formula of an ester is with the acid part first—the reverse of the inorganic method. The full graphical formula for this compound is



or, more simply, CH_3COOCH_3. The process of making an ester, as given above, is called *esterification*, and within certain limits any alcohol and any acid can be made to form an ester.

283 Saponification

These esters are not too stable and rather readily hydrolyze, with water, to form the original alcohol and acid; thus

$$CH_3COO\cdot\boxed{CH_3 + HO}H \longrightarrow CH_3OH + CH_3COOH \quad (120)$$

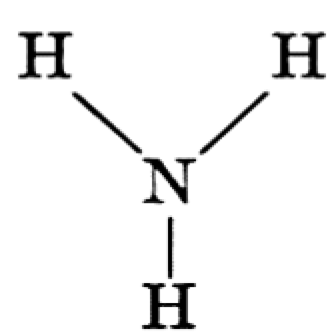
This reversal of esterification is known as hydrolysis; but it is slow and seldom complete. (Read § 184 on hydrolysis.) It can be materially hastened and brought to completion if an alkali is used:

$$CH_3COO\cdot CH_3 + KOH \rightarrow CH_3OH + CH_3COOK \quad (121)$$

In this case instead of the free acid we obtain the potassium salt of it. Since this is in principle the method used with certain other esters called fats for the express purpose of making soaps, this variation of the process of hydrolysis is called *saponification.* It, like hydrolysis, is the reverse of esterification.

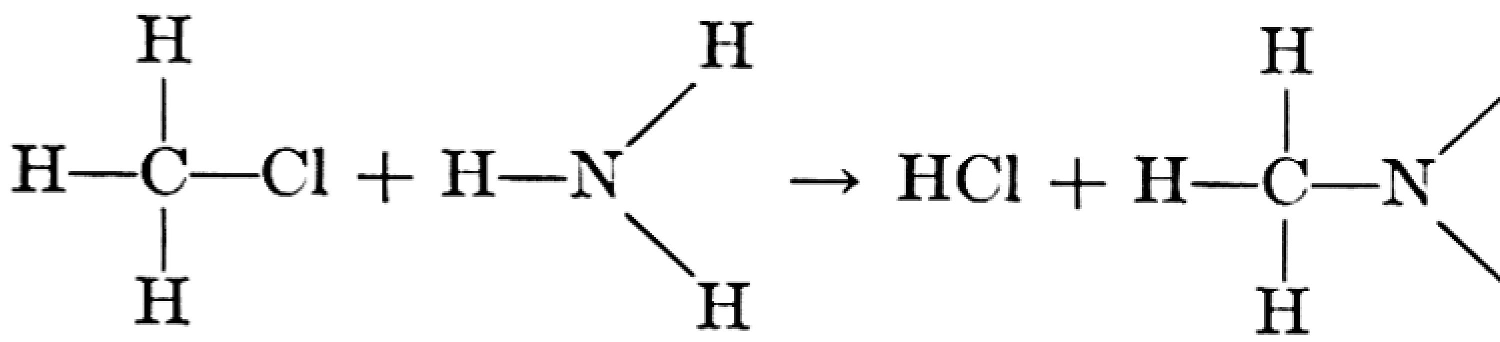
284 Amines

The graphical formula for ammonia is written showing nitrogen to be trivalent and attached to three atoms of hydrogen:



Now if methyl chloride is treated with ammonia, the atom of chlorine is replaced and combines with one atom of hydrogen from the ammonia, forming a molecule of hydrogen chloride. At the same

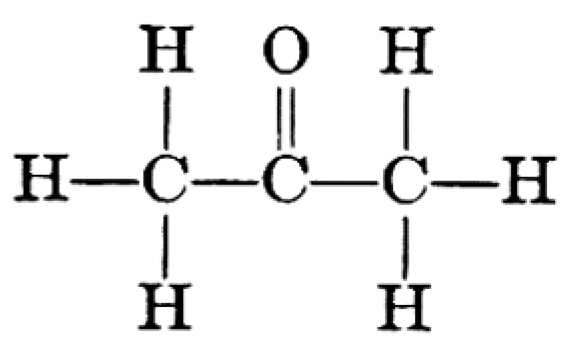
time the methyl radical (CH_3—) connects with the residue of ammonia (NH_2—) to form a molecule of methylamine. Thus


(122)

or $CH_3 \cdot NH_2$ (methylamine). This product is thus a derivative of ammonia, hence the family name *amine.*

285 A Ketone

Another family, of somewhat lesser importance than the preceding ones, may be obtained by decomposition of the acids. Thus by heating two molecules of sodium acetate we may obtain a compound belonging to the family of ketones:


Acetone

written shortly as $CH_3—CO—CH_3$. This is the simplest member of the family of ketones, having as its specific name acetone, since it is derived directly from acetic acid. Its graphical representation, in common with that of aldehydes, shows a carbon atom which is linked by a double bond to an oxygen atom, $>C{=}O$. This accounts for the fact that aldehydes and ketones have many chemical properties in common. But whereas an aldehyde has one hydrogen atom attached to the carbon atom which holds the doubly bound oxygen, a ketone has no such hydrogen; and the carbon atom holding the doubly bound oxygen is attached on each of its two remaining sides to a carbon atom. It is this hydrogen which gives the aldehyde the ability to reduce certain oxidizing agents, getting itself oxidized to the corresponding acid in the process.

This reaction constitutes a test for aldehydes. To about 5 ml of a dilute solution of silver nitrate in a test tube add, drop by drop with shaking, dilute ammonium hydroxide until the light brown coloration at first formed just disappears. Now add a small quantity of an aldehyde, such as a drop of formalin, or acetaldehyde or

grape sugar, and warm gently. In a few moments the solution will darken and a beautiful silver mirror will form in the test tube. This is the *silver mirror test* for aldehydes.

286 Comparisons with Inorganic Compounds

Any family or group of the elements that may be chosen offhand will show certain differences that will permit the members to be identified with relative ease, for example, the halogens; and any number of inorganic solids picked at random will largely resist the action of heat with the exception of ammonium salts and a few others like potassium chlorate. But there is much more physical similarity among all the compounds so far mentioned as organic. For example, methane, ethane (two hydrocarbons), methyl chloride (a halogenated hydrocarbon) and formaldehyde are all gases at ordinary temperatures, and the others are liquids. All are colorless and all are easily vaporized below 150°C. Only the alcohols, acids and acetone are soluble in water, and higher alcohols and acids tend to be quite insoluble. Indeed a very small proportion of carbon compounds is water-soluble, for organic compounds tend rather to dissolve in compounds of their own kind such as hydrocarbons, ethers and esters.

287 Ions in Carbon Compounds

This insolubility in water lends support to the belief that, as a rule, carbon compounds do not form ions in solution as sodium hydroxide or sodium sulfate will when dissolved in water. Their reactions, therefore, will be non-ionic. This statement includes the alcohols which, though, like NaOH, possessing an —OH, will not give any reaction with litmus or phenolphthalein. The reactions of organic acids show that they are very weak, that is, but slightly ionized in aqueous solution. This dissimilarity to inorganic compounds is regarded as due to a different mode of linkage of the electrons when atoms are joined to carbon, either directly or indirectly.

288 Industrial Preparations

In the charting of family connections certain general reactions have been mentioned, by means of which one compound may be prepared from another. Though of importance from the above point of view, it does not follow that these methods of preparation would be either efficient or commercially feasible. In addition, the

small-scale laboratory preparation might represent still another method. An example will serve to illustrate this point. Acetaldehyde is usually prepared in the laboratory by oxidizing ethyl alcohol, using a mixture of potassium dichromate ($K_2Cr_2O_7$) and dilute sulfuric acid, though the heating of sodium acetate (CH_3COONa) with sodium formate ($HCOONa$) will give a small and unsatisfactory yield. The latter method is never employed industrially, and the former would be too expensive. Instead it is manufactured in large quantities by passing acetylene (another gaseous hydrocarbon) into an acid solution in water containing a mercury compound as catalyst. Similarly, the use of silver hydroxide and ethyl chloride to prepare ethyl alcohol would be far from remunerative as long as cheap grains may be fermented. It should be remembered that commercial processes are frequently short cuts, where the source of raw materials and the cheapest methods with the highest efficiency count more toward the production of a marketable commodity than theoretical relationships.

289 Some Homologous Series

To draw attention to the similarities that exist among members of a family, that differ consecutively by increments of CH_2, a few tables are shown below. No one ever tries to memorize the physical properties of organic compounds—there is too much of greater importance—but homologues show with increasing molecular weight a general tendency to escape from the gaseous or liquid to the solid state. This is indicated by their boiling and melting points. At the same time their tendency to enter into chemical reactions decreases as the molecular weight increases. This is a generalization of great importance to organic chemists, who in the same way have discovered that the first member of a series is of abnormally greater chemical activity than the second member. Below are several tables designed to exemplify these principles, a further condensation of graphical formulae being employed to save space, for example, $CH_3(CH_2)_3CH_3$ for $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$, this being a common procedure for large chains of carbon atoms.

290 Homologous Paraffins

The names of these hydrocarbons beyond the fourth show a mixture of Greek and Latin prefixes and end in *ane.* Although compounds to $C_{70}H_{142}$ are known, only one beyond decane is given, and that in order to show its high melting and boiling points.

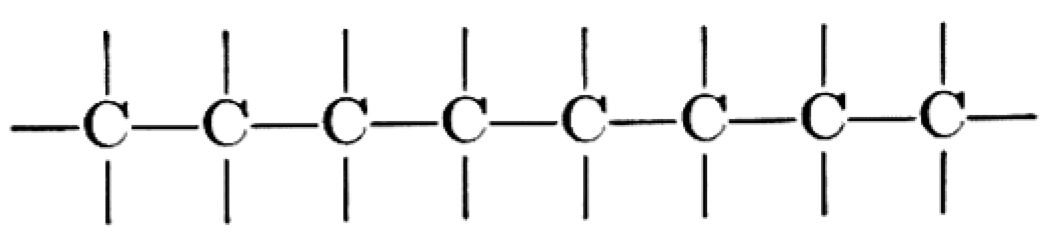
Here it will be seen that, excepting propane, the melting points of the solidified hydrocarbons, and the boiling points of the same compounds when liquid, increase in an orderly manner. The

TABLE 33

THE PARAFFIN HYDROCARBONS

Empirical Formula	Name	Graphical Formula	Melting Point °C	Boiling Point °C
CH_4	Methane	CH_4	−184	−164
C_2H_6	Ethane	$CH_3 \cdot CH_3$	−172	− 89
C_3H_8	Propane	$CH_3 \cdot CH_2 \cdot CH_3$	−190	− 45
C_4H_{10}	Butane	$CH_3(CH_2)_2CH_3$	−135	1
C_5H_{12}	Pentane	$CH_3(CH_2)_3CH_3$	−131	36
C_6H_{14}	Hexane	$CH_3(CH_2)_4CH_3$	− 94	69
C_7H_{16}	Heptane	$CH_3(CH_2)_5CH_3$	− 90	98
C_8H_{18}	Octane	$CH_3(CH_2)_6CH_3$	− 56	126
C_9H_{20}	Nonane	$CH_3(CH_2)_7CH_3$	− 51	150
$C_{10}H_{22}$	Decane	$CH_3(CH_2)_8CH_3$	− 32	173
$C_{18}H_{38}$	Octadecane	$CH_3(CH_2)_{16}CH_3$	28	317

members of this series quoted here can be represented as composed of carbon atoms strung together in chain fashion, for example, octane,



with a hydrogen attached to each empty bond. Such compounds are called *normal* and written as *n*-octane because there are other ways of writing the same number of atoms to represent quite different substances (§§ 299, 300). The melting and boiling points are given in whole numbers.

291 Homologous Alcohols

The alcohols listed are, beyond the fifth, named in the same general way as the hydrocarbons from which they may be prepared. The condensed graphical formulae are of the straight chain type also. They are all seen to be liquids, whose boiling points increase in an orderly manner, the last being inserted because it is the first

TABLE 34

HOMOLOGOUS SERIES OF PARAFFIN-DERIVED ALCOHOLS

Empirical Formula	Name	Graphical Formula	Boiling Point °C
CH_4O	Methyl alcohol	CH_3OH	65
C_2H_6O	Ethyl alcohol	$CH_3 \cdot CH_2OH$	78
C_3H_8O	Propyl alcohol	$CH_3 \cdot CH_2 \cdot CH_2OH$	97
$C_4H_{10}O$	Butyl alcohol	$CH_3(CH_2)_2CH_2OH$	118
$C_5H_{12}O$	Amyl alcohol	$CH_3(CH_2)_3CH_2OH$	138
$C_6H_{14}O$	Hexyl alcohol	$CH_3(CH_2)_4CH_2OH$	156
$C_{12}H_{26}O$	Dodecyl alcohol	$CH_3(CH_2)_{10}CH_2OH$	259

of this long series to exist as a solid under ordinary conditions, its melting point being 24°C.

292 Homologous Acids

Table 35 shows a few of the acids which may be derived from the paraffin hydrocarbons. The names listed are not the most modern

TABLE 35

HOMOLOGOUS SERIES OF PARAFFIN-DERIVED ACIDS

Empirical Formula	Name	Graphical Formula	Boiling Point °C	Melting Point °C
CH_2O_2	Formic acid	$HCOOH$	100	8.5
$C_2H_4O_2$	Acetic acid	$CH_3 \cdot COOH$	118	17
$C_3H_6O_2$	Propionic acid	$CH_3 \cdot CH_2 \cdot COOH$	141	−19
$C_4H_8O_2$	Butyric acid	$CH_3(CH_2)_2COOH$	163	−8
$C_5H_{10}O_2$	Valeric acid	$CH_3(CH_2)_3COOH$	187	−34
$C_6H_{12}O_2$	Caproic acid	$CH_3(CH_2)_4COOH$	202	−1
$C_8H_{16}O_2$	Caprylic acid	$CH_3(CH_2)_6COOH$		16
$C_{10}H_{20}O_2$	Capric acid	$CH_3(CH_2)_8COOH$		31
$C_{12}H_{24}O_2$	Lauric acid	$CH_3(CH_2)_{10}COOH$		44
$C_{14}H_{28}O_2$	Myristic acid	$CH_3(CH_2)_{12}COOH$		54
$C_{16}H_{32}O_2$	Palmitic acid	$CH_3(CH_2)_{14}COOH$		63
$C_{18}H_{36}O_2$	Stearic acid	$CH_3(CH_2)_{16}COOH$		71
$C_{24}H_{48}O_2$	Carnaubic acid	$CH_3(CH_2)_{22}COOH$		74

but are given to show the sources of the acids. Thus butyric from butter; caproic, caprylic and capric from goat's butter particularly; lauric from the laurel tree; myristic from the myrtle; palmitic from the palm; stearic from tallow; and carnaubic from carnauba wax. It is significant that, from butyric onward, all the acids found in natural products of both plants and animals contain an even number of carbon atoms. If the odd-numbered carbon atom acids are required they must be synthesized from one of an even number of carbon atoms. The reason for this is not easy of assignment. Only a few of the boiling and melting points have been given, but they are sufficient to serve as illustrations later on.

293 Nomenclature

A glance at Table 35 will reveal some consistencies as well as inconsistency in nomenclature. Thus the hydrocarbon pentane with five carbon atoms becomes amyl alcohol (since it may be derived from starch for which the Latin is *amylum*). It appears later as valeric acid, which indicates that the acid may be derived from a botanical species including valerian.

The consistency in formulae in each table permits us to adopt certain skeleton formulae to include the members of each homologous series. For example, the paraffin hydrocarbons may be designated by $C_nH_{(2n+2)}$, where n equals any whole number up to 60. If a paraffin hydrocarbon is known to possess thirty-three carbon atoms its formula becomes $C_{33}H_{68}$. Also, the graphical formulae of the alcohols may be still further condensed; $CH_3 \cdot CH_2OH$ may be written shortly as C_2H_5OH and $CH_3 \cdot CH_2 \cdot CH_2OH$ as C_3H_7OH and so on. In this way the alcohols listed in Table 34 may appear as CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$, $C_6H_{13}OH$ and $C_{12}H_{25}OH$. These shortened formulae stress two facts—that the chief constituent of an alcohol is the OH radical or functional group and that the remainder of the molecule is the stem of the corresponding hydrocarbon, the whole hydrocarbon formula less one hydrogen atom. This, then, gives rise to the hydrocarbon radicals —CH_3— from methane, C_2H_5— from ethane, etc., which are known as methyl, ethyl, propyl, butyl, amyl, hexyl and dodecyl. The skeleton formulae for these paraffin radicals may be summarized as $C_nH_{(2n+1)}$, which is equivalent to $C_nH_{(2n+2-1)}$.

Similarly the acids may have their formulae condensed to $HCOOH$, CH_3COOH, C_2H_5COOH, C_3H_7COOH, C_4H_9COOH, etc., for which the skeleton formula becomes $C_nH_{(2n+1)}COOH$.

The alcohols listed in Table 34 are only a few of many known. Therefore, in order to simplify their nomenclature and to include all classes, they are now referred to as *carbinols* with the basic structure $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{OH}$ where the carbon atom may be attached to any three hydrocarbon radicals within wide limits. Likewise, in order to distinguish organic acids from such inorganic ones as hydrochloric and sulfuric, the organic are called carboxylic acids, since they always contain —COOH, which is known as the *carboxyl* radical.

294 Summary of Structures

The vast number of members known to belong to hydrocarbons, alcohols, acids, etc., whether of one homologous series or several, are not really of such importance as we would suppose; for it is the possession of one or more functional groups which determines how a compound will act chemically toward other substances and not so much what they look like or where they boil and so on. It therefore becomes necessary to emphasize the possession of functional groups, and this the organic chemist does by writing them down in strong relief, it being understood that the attachment of hydrocarbon or similar radicals merely draws attention to one specific compound. It cannot be too strongly emphasized that specific compounds mean far less than the families to which they belong. Thus a carboxylic acid always acts as a carboxylic acid with but little respect paid to which one it is. These functional groups, listed below, are always sought out first in seeing a graphical formula for the first time. Furthermore, these functional groups are always sought out first in practice when it is necessary to discover the identity of a newly prepared carbon compound.

295 Review of Characteristic Radicals (or Functional Groups)

There are others besides these shown on this and the following page, but these are the main pictures for identifying new compounds.

Halogen derivatives

$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{Cl}$$

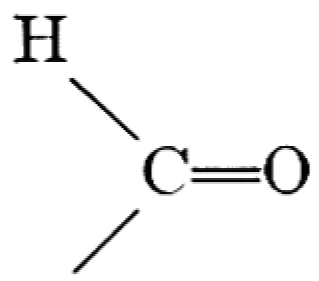
Chlorides

Alcohols

$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{OH}$$

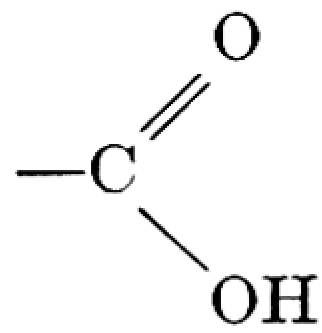
Carbinol group

Aldehydes



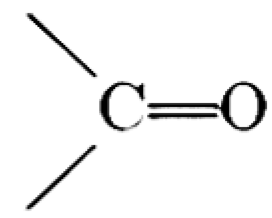
Carbonyl

Acids



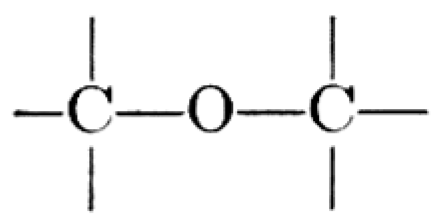
Carboxyl

Ketones



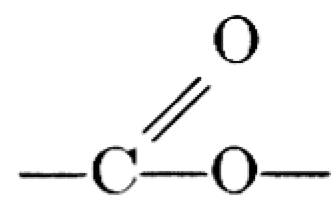
Carbonyl (also)

Ethers



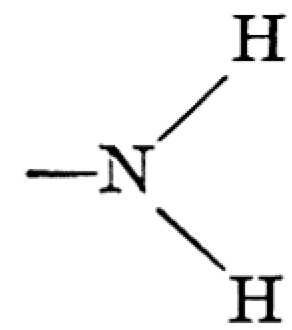
Ether linkage

Esters



Ester linkage

Amines



Amino linkage

296 Review of Definitions

A hydrocarbon is a compound built up of carbon and hydrogen only, for example, methane (CH_4), ethane (C_2H_6).

The halogen derivative of a hydrocarbon is a compound obtained by replacing one hydrogen atom of that hydrocarbon by a halogen atom. Examples are CH_3Cl (methyl chloride, or monochloromethane); C_2H_5Br (ethyl bromide, or monobromoethane).

An alcohol is a compound which contains the hydroxyl radical (OH) attached to a carbon atom, but there must be no other oxygen attached to the same carbon atom, for example, CH_3OH, C_2H_5OH.

An aldehyde is any compound containing the aldehyde radical (—CHO), for example, H—CHO (formaldehyde), CH_3—CHO (acetaldehyde).

An organic acid always contains in its formula the radical —COOH; the hydrogen of this —COOH (carboxyl) is replaceable by a metal or NH_4^+.

An ether is an oxide, where to an oxygen atom (—O—) are attached two hydrocarbon radicals (CH_3, C_2H_5, etc.), which may be the same or different ones. Dimethyl ether (CH_3—O—CH_3) and diethyl ether (C_2H_5—O—C_2H_5) are examples.

An ester is the analogue of an inorganic salt; it is the result of removing the H of a —COOH radical and replacing it by a hydrocarbon radical. $H \cdot COOCH_3$ (methyl formate), $CH_3 \cdot COOC_2H_5$ (ethyl acetate) and $CH_3 \cdot COOC_3H_7$ (propyl acetate) are examples.

Esterification is the process of making an ester; it may be accomplished in several ways, one of which is given in the previous definition.

The term hydrolysis is most frequently used to designate the reaction of a salt with water. Here it means the reaction of an ester (which is an organic salt) with water to regenerate the alcohol and the acid from which that ester may be made.

Saponification is similar to hydrolysis. It is the splitting of an ester with an alkali (NaOH, KOH) to regenerate the alcohol and form the alkali salt (Na, K) of the acid from which the ester was made in the first place.

An amine is a compound in which at least one of the three hydrogen atoms

of ammonia (NH_3) is replaced by a carbon atom with its appropriate hydrogen atoms. Examples are CH_3NH_2 (methyl amine), $C_2H_5NH_2$ (ethyl amine).

A ketone is a compound containing the $>C{=}O$ radical (carbonyl) attached to two hydrocarbon radicals, for example, acetone ($CH_3 \cdot CO \cdot CH_3$).

297 Summary

By a series of reactions involving substitution by a halogen, double decomposition by means of an inorganic hydroxide, oxidation, then further oxidation, and the heating of the sodium salt of an organic acid, a hydrocarbon may progressively give rise to a halogen derivative, an alcohol, an aldehyde, an acid and a ketone.

The above progression may be reversed so that an acid may be prepared from a ketone, an aldehyde from an acid, an alcohol from an aldehyde, a halogen derivative from an alcohol and a hydrocarbon back from the halogen derivative. These two contrary sets of procedures emphasize first the relationships existing among these families of carbon compounds and, second, the ease of chemical transformation of a compound of one family to a compound of another family.

The members of any one family differ consecutively from one another by a constant $—CH_2—$. Such a family becomes known as a homologous series; each member of that family is called a homologue of the others.

Ethers are prepared from two molecules of an alcohol by dehydration.

An ester is obtained from a mixture of alcohol and acid by the elimination of a molecule of water—superficially similar to ordinary salt formation.

Esters are easily hydrolyzed to regenerate the alcohol and acid from which they are formed.

By treating with an inorganic alkali ($NaOH$ or KOH), an ester will give back its alcohol and a sodium salt will be formed. Hydrolysis and saponification are reactions of the same type and each is the reverse of esterification.

Amines may be obtained by replacing the halogen of a halogenated hydrocarbon by means of part of ammonia (NH_3). Amines are really basic substances and will add acids as does ammonia itself.

The addition of magnesium to a halogenated hydrocarbon forms an intermediate compound, for example, $CH_3—Mg—Cl$. This, of the type known as a Grignard reagent, is a very important synthetic compound.

Questions

1. By means of graphical formulae show how acetic acid may be prepared from methane.
2. What do you understand to be meant by the terms paraffin and homologous? Illustrate.
3. How is an ether related to an alcohol? An ester related to both an alcohol and an acid? An amine to ammonia?
4. Illustrate saponification.
5. What is a ketone? How does it resemble an aldehyde?
6. How would you test for an aldehyde?

21

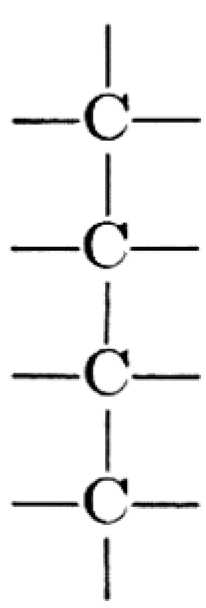
Common Aliphatic Compounds

298 Chains

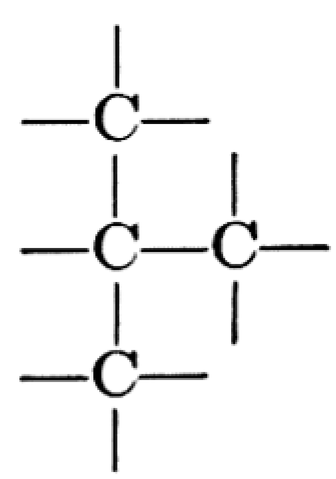
In Chapter 20 we have strung carbon atoms together like links in a chain, always taking care that each carbon atom so linked was properly embellished with hydrogen atoms and, except for paraffin hydrocarbons, with a suitable radical or functional group. It might be of interest to see how otherwise a number of carbon atoms might be linked with respect for the proprieties of valence.

299 Branched Chains

Suppose we have four carbon atoms and ten hydrogen atoms to suit the C_4H_{10} formula of butane. They may be attached in these two ways:



I



II

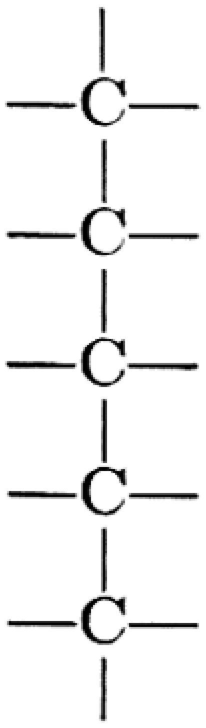
In I no one carbon atom is directly attached to more than two other carbon atoms, whereas in II there is one carbon atom holding as many as three carbon atoms. A brief glance will show as many positions in I to attach monovalent hydrogen atoms as in II, so that both pictures could represent butane.

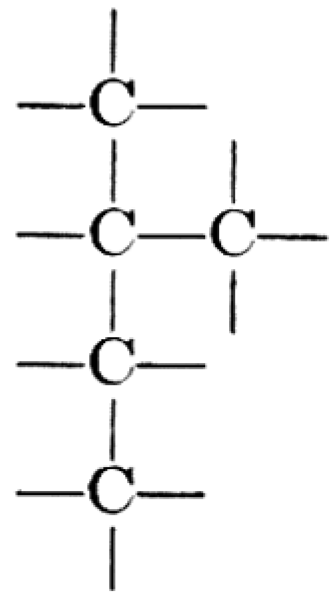
300 Isomerism

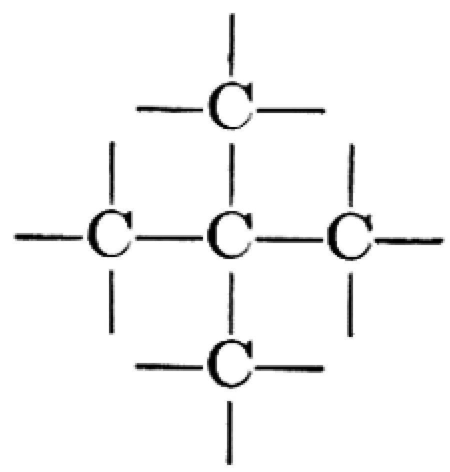
If this picture-drawing business is legitimate, there should be two butanes; and there are. The proof is unnecessary here, but I

is the carbon linkage of *normal* butane, written *n*-butane, and II is the mode of linkage in *isobutane*. Their physical properties are *n*-butane, melting point −135°C, boiling point 1°C; isobutane, melting point −145°C, boiling point −10°C.

Another example may be taken from C_5H_{12}, formerly mentioned as pentane. It may be written in three ways:


I


II


III

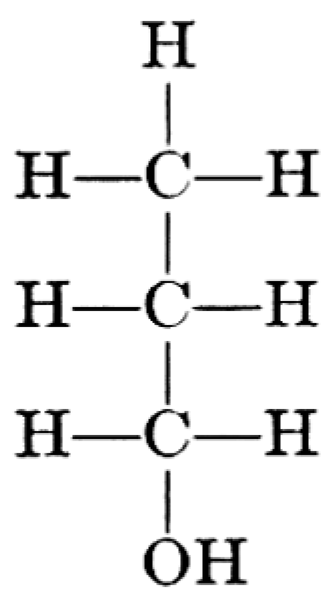
Again, if our premises are correct, there should be three pentanes. I would represent the ordinary chain mode of linkage and the hydrocarbon called *n*-pentane; II is the first variant and might be termed isopentane; III gives rise to what has been named neopentane. There are three pentanes as illustrated by their physical properties: *n*-pentane, melting point −131°C, boiling point 36°C; isopentane, melting point −160°C, boiling point 28°C; neopentane, melting point −20°C, boiling point 9°C.

If we consider the two butanes we find that we are dealing with two distinct chemical compounds, the normal or straight chain, and the iso or branched chain. Their physical properties are so different as to suggest that they are different chemically also, yet their atoms are the same in number with a consequent identity in molecular weight. The existence of two or more compounds possessing the same number and kind of atoms but different properties and mode of behavior is called *isomerism*. It is likewise exemplified by the pentanes, whose three structures imply the existence of three different compounds included in the empirical formula C_5H_{12}. Indeed, this isomerism becomes more involved as we go on, so that the number of paraffin hydrocarbons from C_1 to C_{60} actually runs into the millions, relatively few of which it has ever been thought necessary to synthesize. Natural petroleum contains a huge number of them, so many that it has been found impossible

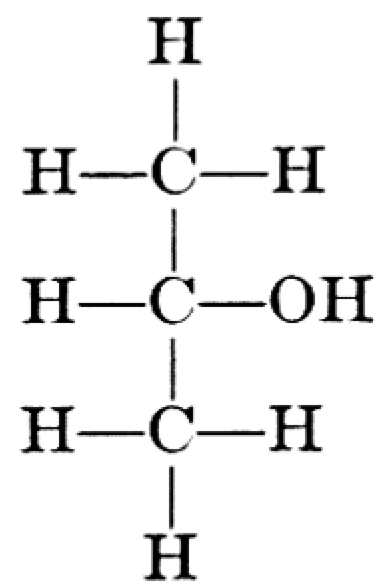
to separate them by distillation methods. Gasoline, one fraction of distilled petroleum oils whose average boiling point makes it of such use in internal-combustion engines, is a mixture of the C_5 to C_9 hydrocarbons. It is now apparent why so much insistence was laid on graphical formulae at the beginning of this organic part of the book, for it does really make a difference where atoms are linked in carbon compounds in contrast to the usual run of inorganic compounds.

301 Isomerism Is Widespread

Nor is this isomerism confined to hydrocarbons, for propyl alcohol affords a similar example. The propyl alcohol given in Table 34 is called normal; but C_3H_8O may be written in two ways:



I



II

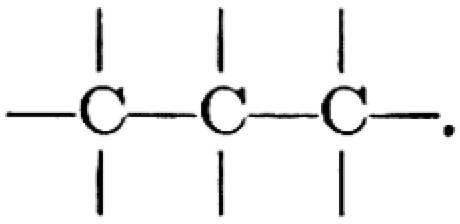
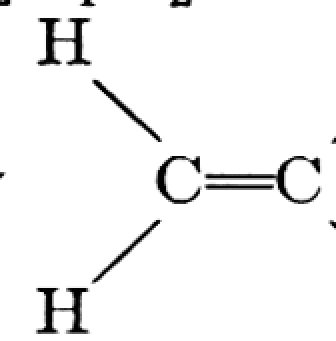
where I has the hydroxyl OH attached to an end carbon atom and in II it is found on the middle one. That their physical properties differ is shown by the fact that, whereas the melting and boiling points of I (*n*-propyl alcohol) are −127°C and 97°C, respectively, the analogous figures for II (isopropyl alcohol) are −86°C and 81°C. The oxidation of both these compounds gives different results, the normal alcohol producing propionic aldehyde, and the iso compound acetone. Thus chemically as well as physically we have two isomeric propyl alcohols.

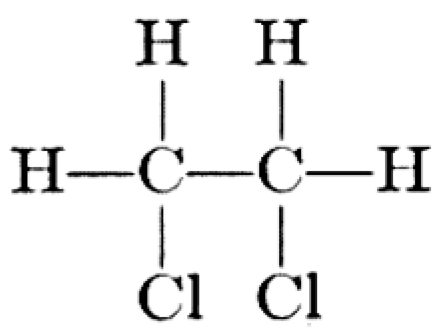
Inspection of the formula C_2H_6O suggests that ethyl alcohol is written as $CH_3 \cdot CH_2OH$; it may also suggest $CH_3—O—CH_3$, which is dimethyl ether, an altogether different compound and of another family besides. Isomers may therefore include all families of compounds as long as the requirements of the same molecular weight and different properties are maintained.

302 Constitution and Formula

Moreover, graphical formulae are seen now to express more than the composition of a molecule. They also tell its constitution or configuration, and hence are called constitutional formulae for purposes of distinguishing them from the empirical or compositional formulae.

303 Unsaturated Hydrocarbons

Having gained an insight into the structure of some members of the commoner carbon compounds, we may now proceed to somewhat more complex examples. Looking back over those we have studied, we may recall that all the graphical formulae displayed showed the carbon atoms joined each to the next by a single bond, . Now if ethyl alcohol is dehydrated by means of, say, concentrated sulfuric acid or dry alumina at temperatures above that for the formation of diethyl ether, a gas will be produced whose analysis and molecular weight give it a formula of C_2H_4, two hydrogen atoms short of ethane. This gas is far more reactive chemically than ethane, for it adds two atoms of chlorine per molecule to give a compound $C_2H_4Cl_2$. It is called ethylene and has the structure indicated by , the addition of chlorine giving ethylene dichloride (or dichloroethane):



Ethylene is the first of another homologous series of hydrocarbons known as the ethylenes or olefines, which differ from the paraffins in that they possess a pair of carbon atoms joined by double bonds instead of by single bonds. The skeleton formula to represent them is C_nH_{2n}, and their names are taken from the paraffins in the following manner: ethane, ethylene; propane, propylene; butane, butylene and so on.

A further type of hydrocarbon is acetylene, C_2H_2, which is easily prepared by dropping pieces of calcium carbide into water:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow \qquad (123)$$

This is a gas, more reactive still than ethylene and capable of adding four atoms of chlorine to give tetrachloroethane ($C_2H_2Cl_4$). Acetylene ranks high as a source of organic compounds. In order to express its structure in terms of its reactions and formula, the carbon atoms must be joined by a triple bond, H—C≡C—H.

304 Hydrogenation of Unsaturated Hydrocarbons

By a process of hydrogenation, that is, adding elementary hydrogen to molecules, usually in the presence of a suitable catalyst such as nickel or palladium, acetylene can be converted to ethylene, and ethylene to ethane.

$$C_2H_2 + 2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6 \qquad (124)$$

The fact that hydrogen and other elements can be added to acetylene and ethylene indicates that these two hydrocarbons are not saturated, that is, the carbon atoms can hold more by changing to the single-bond mode of linkage. Hence all compounds of this nature which can so add on other elements (or even compounds) are called unsaturated.

As with methane and ethylene, acetylene is the first of another homologous series of hydrocarbons whose skeleton formula is $C_nH_{(2n-2)}$. All three series have their related halogen derivatives, alcohols, aldehydes, acids, etc., as illustrated by the paraffins.

305 Aliphatic Compounds

These three series and their combinations constitute what is called the aliphatic compounds to distinguish them from those which have their carbon atoms joined in a ring-like manner and are called cyclic. Derivatives of the aliphatic hydrocarbons are frequently referred to as *alkyl*; those of the cyclic type are called *cycloalkyl* (if aromatic, *aryl*).

306 Methyl Alcohol

In succeeding pages some of the more generally used aliphatic compounds are described. The first of them is methyl alcohol

(CH_3OH), commonly known as wood spirit since it was long prepared by the destructive distillation of wood (§ 474). This method is now largely superseded by combining the constituents of water gas:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (125)$$

Though toxic to animals, producing blindness, methyl alcohol is largely used as a solvent for organic compounds and as a starting point for the synthesis of more complex substances.

307 Formaldehyde

Methyl alcohol may be oxidized to give formaldehyde ($HCHO$), a gas whose 40 per cent solution in water is used as a disinfectant under the name of formalin. Formaldehyde, in addition, is made to combine with phenolic compounds (§ 517) to produce synthetic resins whose application to industry during the past generation has been of such outstanding importance.

308 Acetic Acid

Acetic acid is now chiefly prepared from acetylene, though formerly produced from wood along with methyl alcohol. Large quantities of acetic acid (CH_3COOH) and anhydride [$(CH_3CO)_2O$] are required in the manufacture of cellulose acetate for various purposes (§ 480).

309 Carbon Tetrachloride

Carbon tetrachloride (CCl_4), a heavy, volatile and non-inflammable liquid, can be made by the chlorination of methane. It is an excellent solvent for oily substances and is also used as a fire extinguisher. Partial reduction of carbon tetrachloride produces chloroform ($CHCl_3$), a heavy, sweet liquid, volatile and non-inflammable. It was formerly employed as a general anesthetic, but has been replaced by diethyl ether [$(C_2H_5)_2O$], the sulfuric ether of commerce.

310 Ether

This is a very volatile liquid, with a sweet but pungent odor. It is a valuable solvent whose chief drawback is its great inflammability.

311 Ethyl Alcohol

Ethyl alcohol (C_2H_5OH), or grain alcohol, may be prepared by fermenting barley or corn. It is used as a drink when suitably matured, is denatured with methyl alcohol, brucine, benzene, etc., to make it unfit for drinking but suitable for other purposes. Large quantities are used industrially to manufacture other compounds, among which is ethyl acetate ($CH_3COOC_2H_5$), a sweet-smelling liquid with important solvent characteristics.

312 Mixing the Radicals

So far, in our consideration of the paraffin hydrocarbons and their related compounds, we have met only those families in which the radicals —OH, —CHO, —COOH occur only once. We now come to consider a few of the important compounds which contain two such radicals.

313 Glycol

It is represented by

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

where on each of two carbon atoms we have an —OH group. Such compounds are dialcohols, or dihydroxy alcohols, commonly known as glycols, the simplest member of which is pictured above. This substance behaves as an alcohol, but twice so, having twice the reactions of a compound possessing but one OH group. Its low freezing point, high boiling point and miscibility with water make it of advantage as an anti-freeze; it is also a poison.

314 Oxalic Acid

Here we have two —COOH groups joined together,

$$\begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Oxalic acid is found in nature usually as the calcium salt, and is the double oxidation product of glycol. It is a dibasic acid and poisonous if taken internally. Dialdehydes, diketones, etc., are known, but are of little importance here.

Similarly we have hydroxy aldehydes, hydroxy acids, hydroxy ketones, hydroxy ethers, aldehydic acids, etc.—a great variety of compounds.

315 Glycerol

In the same way we may have three and more of these different radicals attached to the carbon atoms of our paraffins. Of them the most important is the trialcohol glycerol, whose formula is

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Its importance lies in the fact that it is the alcohol which, in combination with certain acids, gives rise to fats.

316 Nitroglycerin

If glycerol is treated with a mixture of nitric and sulfuric acids, the trinitrate is obtained:

$$\begin{array}{lclcl} CH_2OH & & HNO_3 & & CH_2—NO_3 \\ | & & & & | \\ CHOH & + & HNO_3 & \rightarrow & CH\ —NO_3 + 3H_2O \\ | & & & & | \\ CH_2OH & & HNO_3 & & CH_2—NO_3 \end{array} \qquad (126)$$

This is generally known as nitroglycerin, a misnomer as it is merely the nitric acid salt (or ester) of glycerol, that is, glycerol trinitrate.

317 Fat Acids

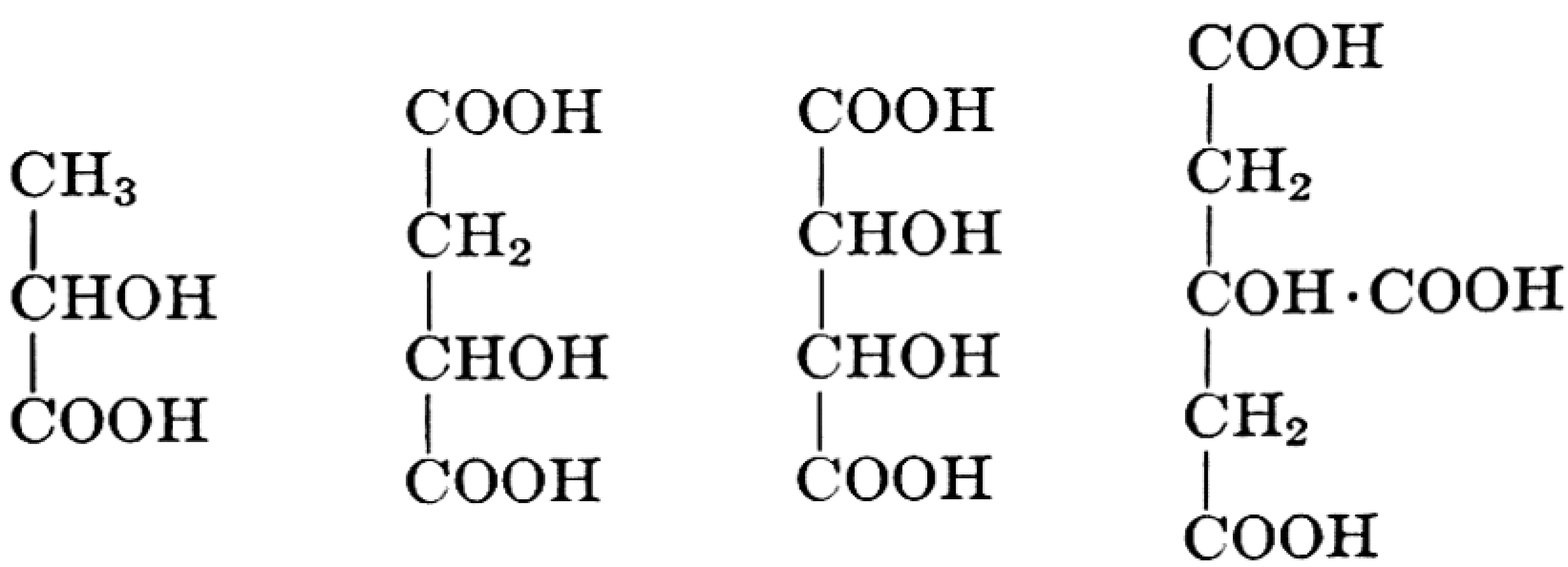
Combined with glycerol in natural fats are such acids as butyric, caproic, caprylic, capric, lauric, myristic, palmitic and stearic (see Table 35). In addition we find oleic, linoleic and linolenic acids, whose formulae represent increasing loss of hydrogen by comparison with stearic: stearic, $C_{17}H_{35}COOH$; oleic, $C_{17}H_{33}COOH$; linoleic, $C_{17}H_{31}COOH$; linolenic, $C_{17}H_{29}COOH$. This means that oleic acid possesses one double bond or ethylene linkage $\left(\begin{array}{c} \diagdown \quad \diagup \\ C{=}C \\ \diagup \quad \diagdown \end{array} \right)$ in its molecule, representing a deficiency of two hydrogen atoms compared with stearic acid; linoleic possesses two such linkages, and linolenic three.

318 Sugars

Certain other types of compounds are widely distributed in natural products. Among them the hydroxyl radical figures largely, especially when associated with the aldehyde or ketone (carbonyl) radicals. Prominent examples are the simple sugars, such as glucose (also known as dextrose and grape sugar) and fructose, also known as levulose or fruit sugar. Their simplified formulae are, respectively, $CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CHO$ and $CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot CO \cdot CH_2OH$. Each of them is five times an alcohol and once an aldehyde or ketone.

319 Fruit Acids

In addition to fruit acids, and frequently accompanying them in the juice of fruits, we find such combinations of the hydroxyl and carboxyl radicals as malic, tartaric and citric acids; the milk of mammals contains the simpler lactic acid. Their formulae illustrate their constitution:



Lactic acid — Malic acid — Tartaric acid — Citric acid

These names indicate their first discovered source: lactic from milk (Latin, *lac*), malic from the apple (Latin, *malum*), tartaric (French, *tartre*), since this acid was first isolated from French wines, and citric from the citrous fruits. These acids occur in larger proportion in the unripe than in the ripe fruits. They are weak acids, and in the alimentary tract they are very easily oxidized to carbon dioxide and water.

320 Review of Definitions

Isomerism is the phenomenon displayed by two (or more) compounds which possess the same kinds of atoms, the same number of each type and the same molecular weight, but show different physical and chemical properties. These compounds are called isomers.

Isomers may belong to the same family (or series), for example, butane and isobutane, or to different families, for instance, acetic acid (an acid) and methyl formate (an ester of methyl alcohol and formic acid).

Paraffin hydrocarbons may be graphically formulated, and these formulae show all the carbon atoms joined to one another by single bonds. Compounds so formed are called saturated, that is, the carbon atom valences hold all they can (compare with saturated solutions).

But when carbon atoms are joined by more than one bond

$$\left(\begin{matrix} \diagdown & & \diagup \\ & C{=}C & \\ \diagup & & \diagdown \end{matrix} \quad \text{or} \quad -C{\equiv}C- \right)$$

the compounds containing these linkages are termed unsaturated.

Ethylene is the first hydrocarbon to contain a double bond; it is therefore an unsaturated hydrocarbon and the first member of a new series of hydrocarbons —the ethylenes (formerly called olefines).

Acetylene is also the first of a third series of hydrocarbons. It is unsaturated, and its graphical formula contains a triple bond.

Hydrogenation is a term most commonly employed to indicate the addition of hydrogen atoms to double and triple bonds as in compounds of ethylene and acetylene.

Aliphatic is the general term used to describe compounds whose graphical formulae involve chains of carbon atoms, whether they are straight or branched chains.

321 Summary

The possibility of different modes of linking atoms together affords an explanation of isomerism.

Although the paraffin hydrocarbons with their single carbon linkages are capable only of substitution, compounds which contain doubly or triply bound carbon atoms can add other atoms like hydrogen, the halogens, etc.

Just as the paraffins have their homologous series (plural) of alcohols, aldehydes, etc., so the ethylenes and acetylenes have theirs. All are included under the general term aliphatic compounds. They are carbon chain compounds.

The addition of sufficient hydrogen atoms (two for a double bond and four for a triple bond) converts ethylene and acetylene compounds to paraffin-derived compounds.

Carbon compounds are not restricted to one radical (or functional group): glycol ($CH_2OH \cdot CH_2OH$) is twice an alcohol; oxalic acid ($COOH \cdot COOH$) is twice an acid (compare sulfuric acid); glycerol [$C_3H_5(OH)_3$] is thrice an alcohol [compare $Al(OH)_3$].

Mixed radicals may occur in a formula, for example, lactic, malic, tartaric and citric acids.

Fats are esters of the alcohol glycerol and acids, usually with long chains of carbon atoms. These acids are therefore called fat acids.

Fats may be hydrolyzed to give glycerol and the various fat acids charac-

teristic of the source which produces such fats. These acids may be saturated (palmitic, stearic) or unsaturated (oleic, linoleic, etc.).

Sugars are hydroxy aldehydes or hydroxy ketones. They are a subdivision of carbohydrates (Chapter 24).

Questions

1. Illustrate straight chain and branched chain compounds.
2. What is meant by isomerism? Illustrate.
3. Write full graphical formulae for methyl, ethyl, propyl and isopropyl alcohols.
4. Write full graphical formulae for methyl acetate, propyl propionate, *n*-butyl formate, methyl propyl ether, ethane, ethylene, acetylene, acetaldehyde, acetone, formaldehyde, glycerol.
5. How do paraffin and ethylene compounds differ in structure?

22

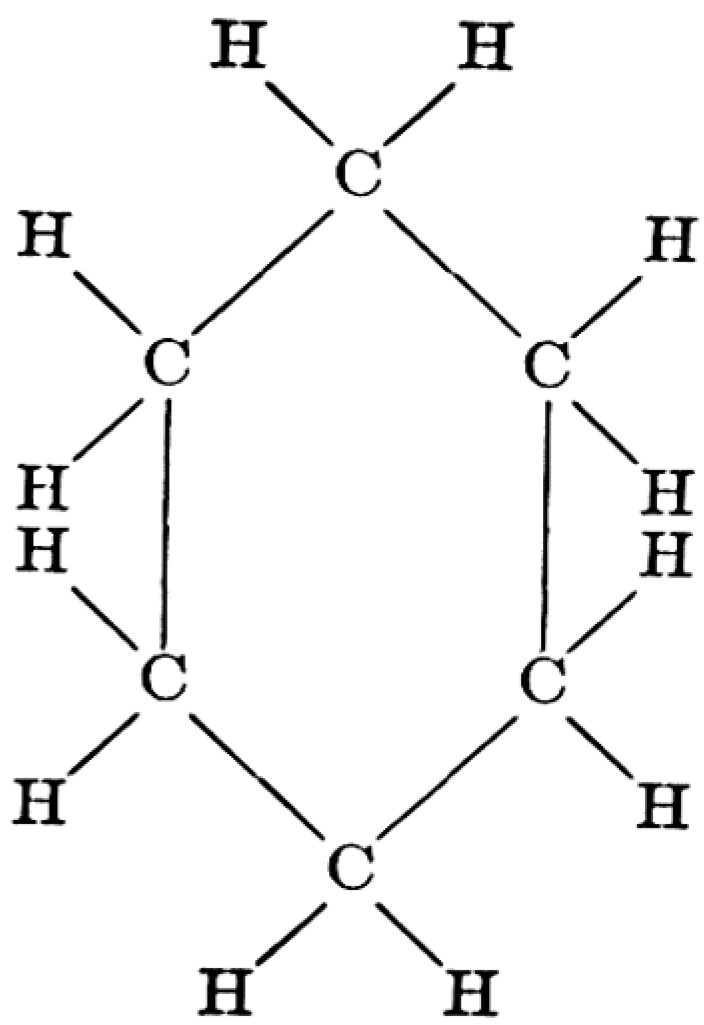
Cyclic and Aromatic Compounds

322 Cyclohexane

So far all the organic compounds presented have been of either the straight or the branched chain type and are grouped together as aliphatic substances. The compounds to be studied in this chapter are examples of the closed chain or ring type. A simple experiment will illustrate how a chain compound may be converted into a ring. The dichlorohexane, which has one chlorine atom at each end of the chain,

$$ClCH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Cl$$

may be treated with metallic zinc, which removes both the chlorine atoms to form zinc chloride ($ZnCl_2$). Consequently, the two end carbon atoms join together. The picture is now a regular hexagon of carbon atoms, each of which holds two atoms of hydrogen:



This is known as a ring or cyclic compound, and the formula above is that of cyclohexane, also called hexamethylene (methylene =

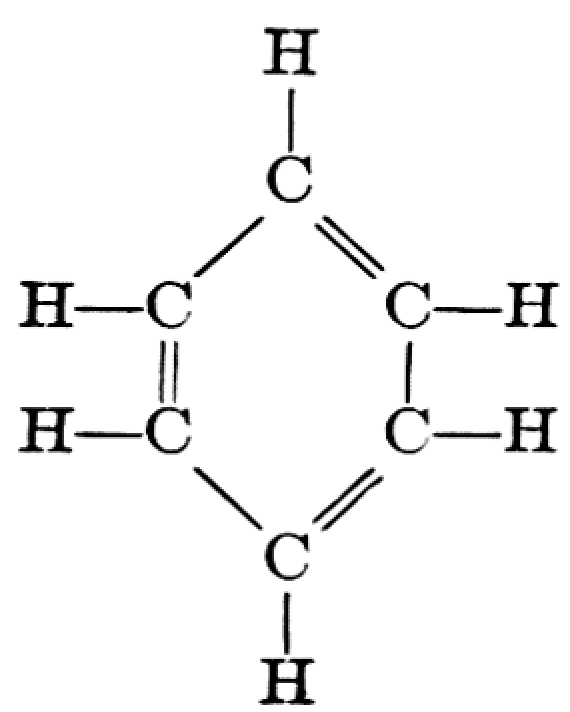
—CH_2—). Similar rings of three, four, five, seven or more carbon atoms may be made, although the first two are less stable than the larger rings.

It will be observed that only single bonds exist between any pair of carbon atoms in the above formula, just as in the paraffins. These cyclic bodies are therefore saturated like the paraffins, and unlike the ethylenes and acetylenes. They have their homologues, additional carbon atoms taking the place of one or more hydrogen atoms of the ring, and these homologues show, therefore, a great variety of isomers. Cyclic hydrocarbons have their halogen compounds (by substitution), their alcohols, aldehydes, etc., just as the other three classes of hydrocarbons studied.

They do not, however, constitute so important a group of compounds as those which have gone before or those which follow.

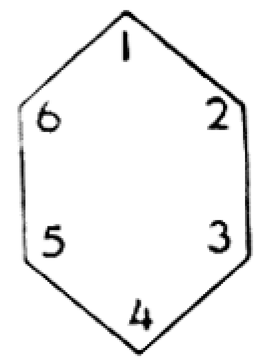
323 Benzene

Of far greater interest than the cycloparaffins (polymethylenes) is that series to which the name aromatic has been given. And just as the former may be obtained by appropriate treatment of the paraffins, so the aromatic compounds may be synthesized from simple chain compounds. If a stream of acetylene is passed through a hot tube, some of the gas is converted into a compound having the formula C_6H_6. This is a ring compound, and because of its physical and chemical properties it has been assigned the accompanying formula



where the carbon atoms are alternately linked by single and by double bonds. It is benzene, the first member of the aromatic series.

For purposes of convenient representation the formula we shall employ is a hexagon slightly elongated:



Beginning at the top and going clockwise, we put a number at each angle; at each angle is a carbon atom with one hydrogen atom attached, although not shown.

The representation of benzene by a plain hexagon suggests that the double bond existing between each alternate pair of carbon atoms has not the significance of such a bond as it occurs in the ethylenic compounds. This is quite true, for benzene does not show the tendency to add atoms that we might expect by comparison with ethylene (§ 303). Indeed, in many of its reactions benzene may be considered to be as saturated as cyclohexane. To show its relation to cyclohexane, benzene may be hydrogenated easily; whereupon it adds on six hydrogen atoms, one to each carbon atom, and the result is cyclohexane. Table 36 shows some points of comparison among *n*-hexane, cyclohexane and benzene.

TABLE 36

PHYSICAL PROPERTIES OF *n*-HEXANE, CYCLOHEXANE AND BENZENE

Property	*n-Hexane*	*Cyclohexane*	*Benzene*
Formula	C_6H_{14}	C_6H_{12}	C_6H_6
Mol. weight	86	84	78
Melting point	−94°C	6°C	5°C
Boiling point	69°C	81°C	80°C
Density	0.660	0.779	0.878

Though in melting and boiling points benzene and cyclohexane are very similar, the density of benzene points to its having a much more compact molecule. Its compactness is likewise responsible for its ability to refract light.

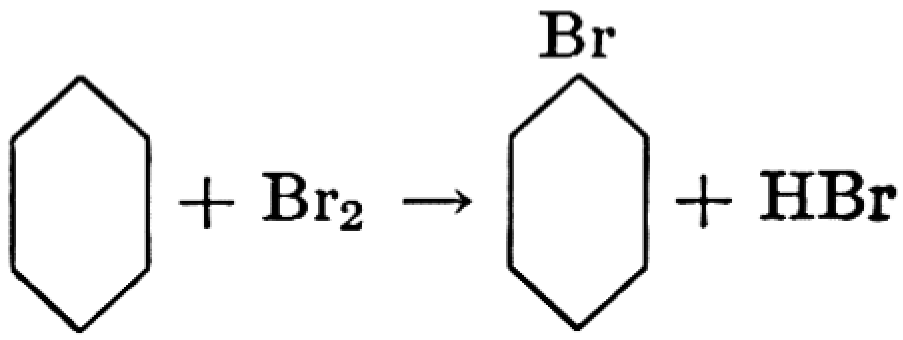
324 Coal the Source of Aromatic Hydrocarbons

The chief source of benzene (as well as of some of its homologues) is bituminous coal, from which it is obtained by destructive distilla-

tion. Its use is of rather recent date when it is considered that coal gas, produced in the same manner, has been used for street lighting for over a century and a half. Benzene was at one time counted among the useless by-products of bituminous coal treatment and discarded. The discovery of methods of synthesizing dyes from benzene late in the nineteenth century naturally changed all that.

325 Substituting in Benzene

Benzene is so important industrially and can give rise to such a huge number of valuable compounds that some knowledge of its versatility is appropriate. Taking the hexagon as representing a molecule of benzene, and adding to it a bromine molecule, we find that one bromine atom replaces one hydrogen atom of the benzene molecule, the other bromine atom forming hydrogen bromide. This is an example of substitution, so common among the paraffins:

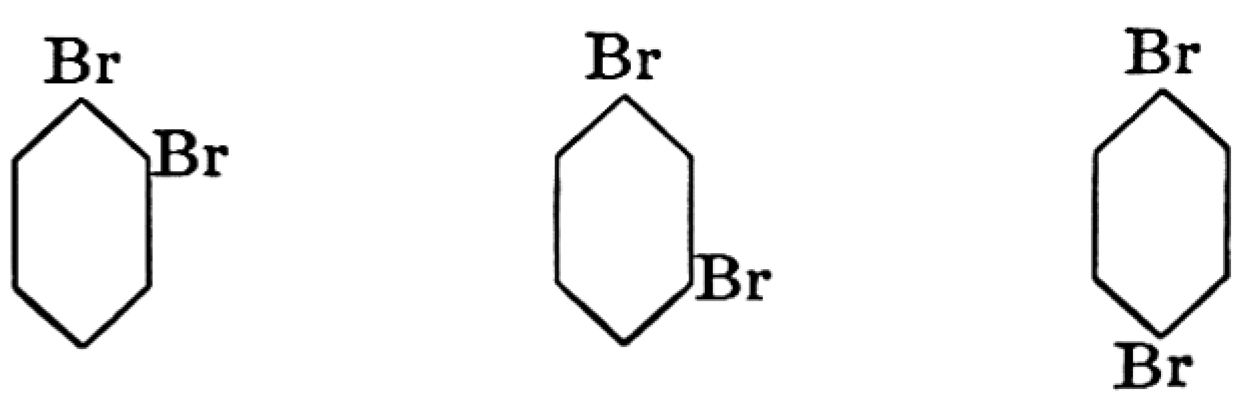


(127)

The resulting compound (C_6H_5Br) is usually known as bromobenzene, although the name phenyl [1]·bromide is also used. It does not matter where one such bromine atom is attached although we prefer to begin at the top carbon atom of our hexagon.

326 Isomerism in Benzene Compounds

But when we replace two hydrogen atoms by bromine to obtain empirically $C_6H_4Br_2$, we find that this formula answers to the composition of three different isomers. These isomers are shown below:



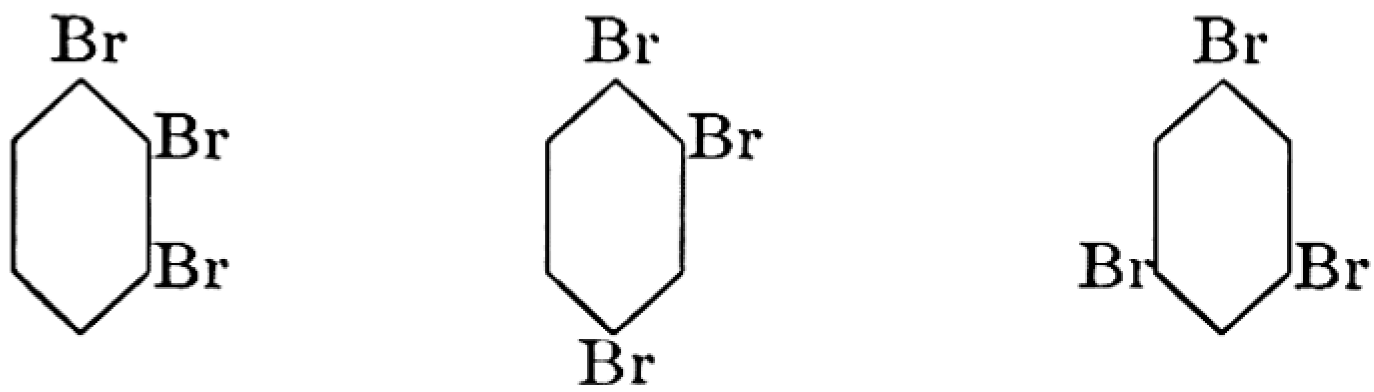
o *m* *p*

and are known as ortho-, meta-, and para-dibromobenzene, or *o*-, *m*-, and *p*-dibromobenzene. That is, when two radicals substi-

[1] The C_6H_5 radical is known as *phenyl*.

tute in the benzene ring (or nucleus, as it is commonly called), there are three different positions that these substituents may occupy: (1) ortho, on adjacent carbon atoms; (2) meta, on alternate carbon atoms; (3) para, on opposite carbon atoms. If we number the positions as indicated above, 1,2 may be substituted for the prefix ortho, 1,3 for meta and 1,4 for para.

With three substituents there are three compounds possible, as follows:

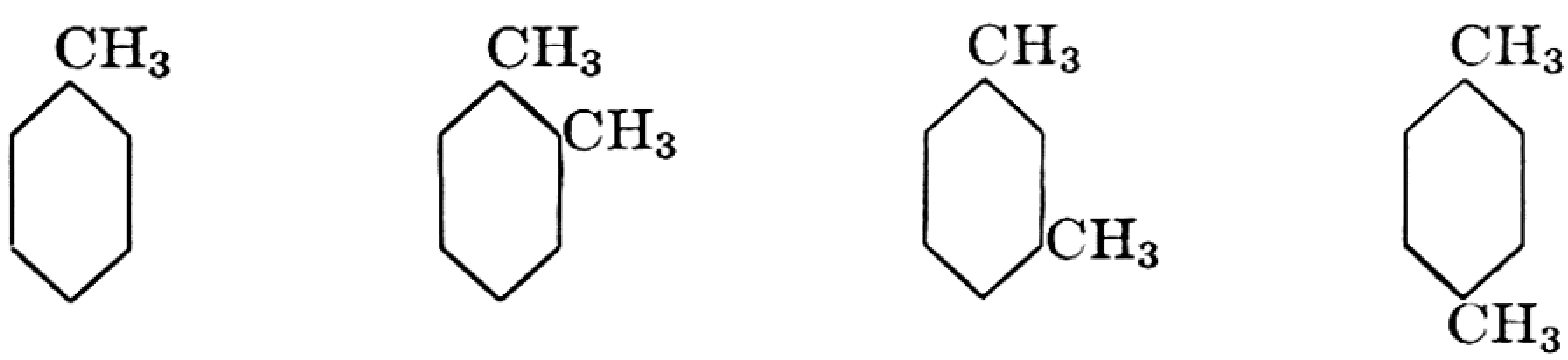


1,2,3 1,2,4 1,3,5
Tribromobenzenes

In complex cases of substitution we use numerals altogether to indicate the correct positions. There are thus many possible isomers of benzene compounds.

327 Homologues of Benzene

Among the homologues we have toluene and the three xylenes, ortho-, meta- and para-:



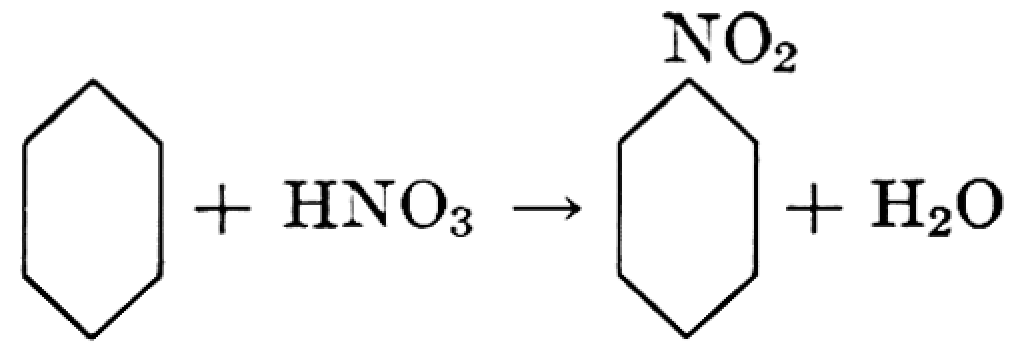
Toluene *o*-Xylene *m*-Xylene *p*-Xylene

Toluene may also be written shortly as $C_6H_5 \cdot CH_3$.

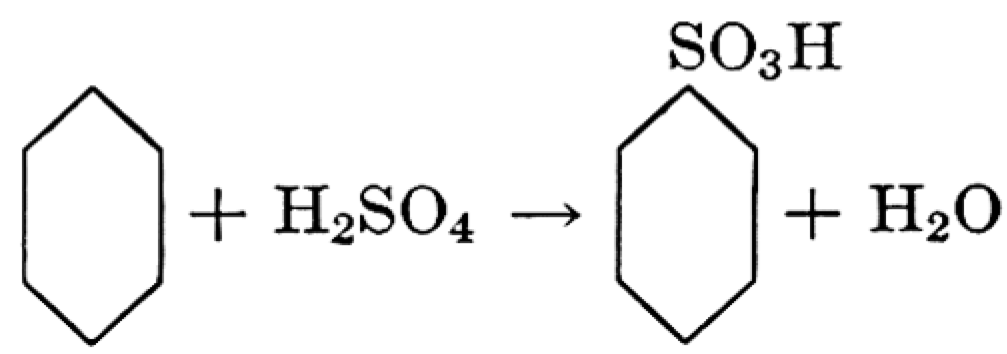
In looking at the formula of toluene we see part of the benzene nucleus and part of methane; in fact toluene may be made in a manner analogous to the formation of ethane from methyl chloride. Toluene behaves to different chemical reagents according to these two parts, the aliphatic CH_3— radical whose reactions are those of methane, and the aromatic C_6H_5— radical with almost entirely different reactions. For example, the CH_3— is susceptible to the action of the halogens and oxidizing agents only; whereas sulfuric and nitric acids readily react with the benzene nucleus and not with the methyl portion.

328 Nitration and Sulfonation

A few of the most important reactions of benzene may be illustrated as follows:



Benzene Nitrobenzene (128)

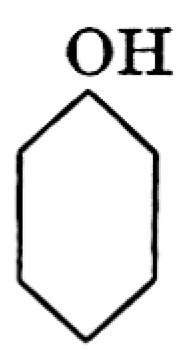


Benzene Benzenesulfonic acid (129)

So in the benzene picture we may for one hydrogen substitute —NO_2 or —SO_3H, or more of these radicals for more hydrogen atoms.

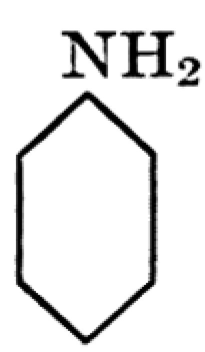
329 Aniline and Phenol

These particular compounds are important only because they are intermediate bodies in the production of more interesting ones. For example, treating benzene sulfonic acid suitably with sodium hydroxide we obtain phenol (C_6H_5OH), commonly called carbolic acid, the disinfectant:



Phenol

Similarly from nitrobenzene we may, by reduction, obtain aniline ($C_6H_5NH_2$), the starting point in the preparation of many dye substances:



Aniline

Aniline is an amine with all the chemical reactions of amines, whereas phenol, though resembling an alcohol according to its

formula, is in reality more like an acid. It is not readily oxidized, nor does it easily form esters when combined with acids.

Related to toluene ($C_6H_5 \cdot CH_3$) we have a true alcohol, benzyl alcohol ($C_6H_5 \cdot CH_2OH$); the aldehyde, benzaldehyde ($C_6H_5 \cdot CHO$) with the odor of bitter almonds; and benzoic acid ($C_6H_5 \cdot COOH$).

330 A Simple Aromatic Chart

The reactions of benzene lend themselves to charting similar to the method previously employed for compounds of the paraffins; this is illustrated in Fig. 66.

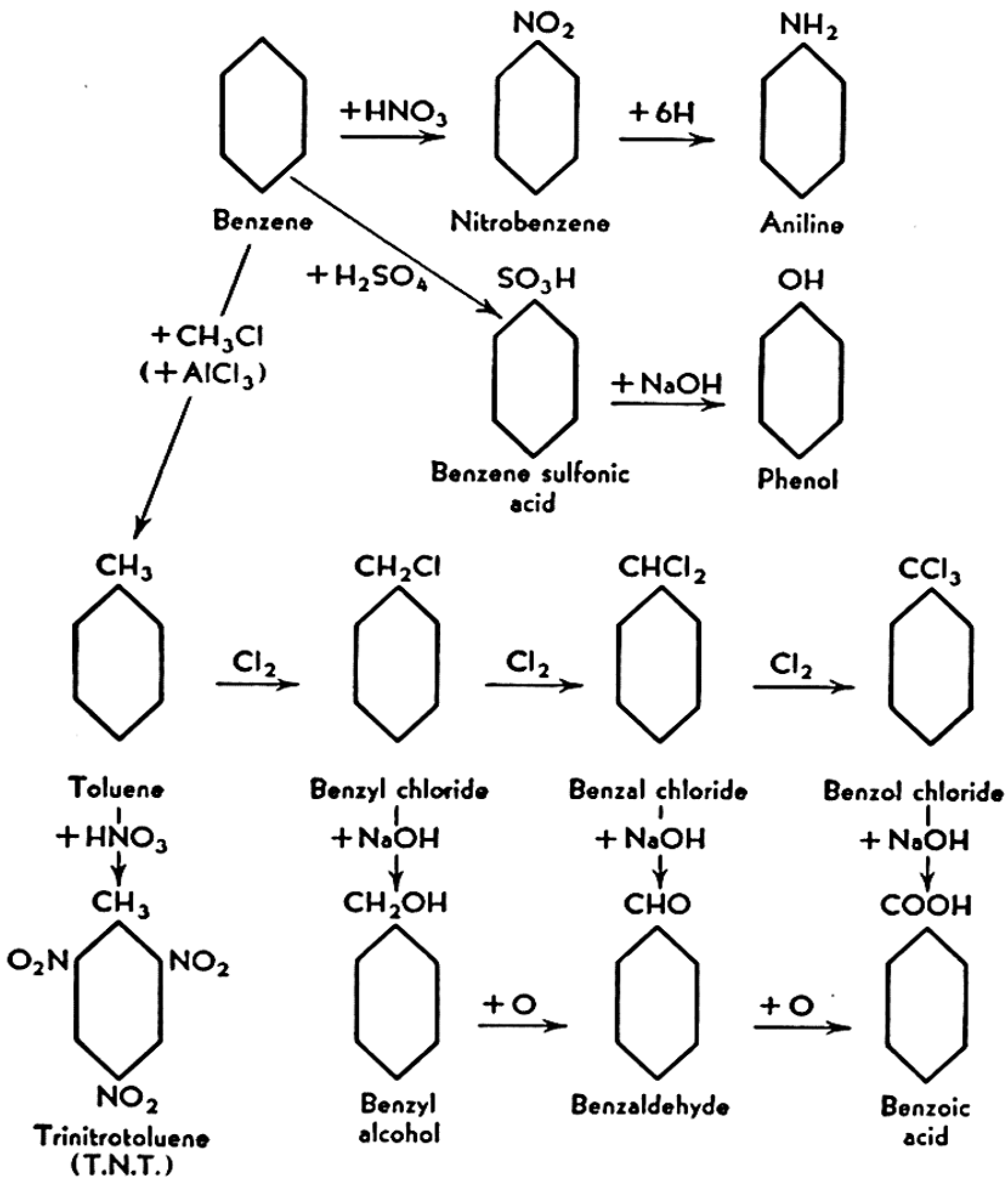
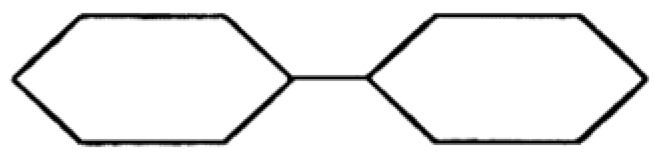


FIG. 66. Synthetic interrelationship of some aromatic compounds.

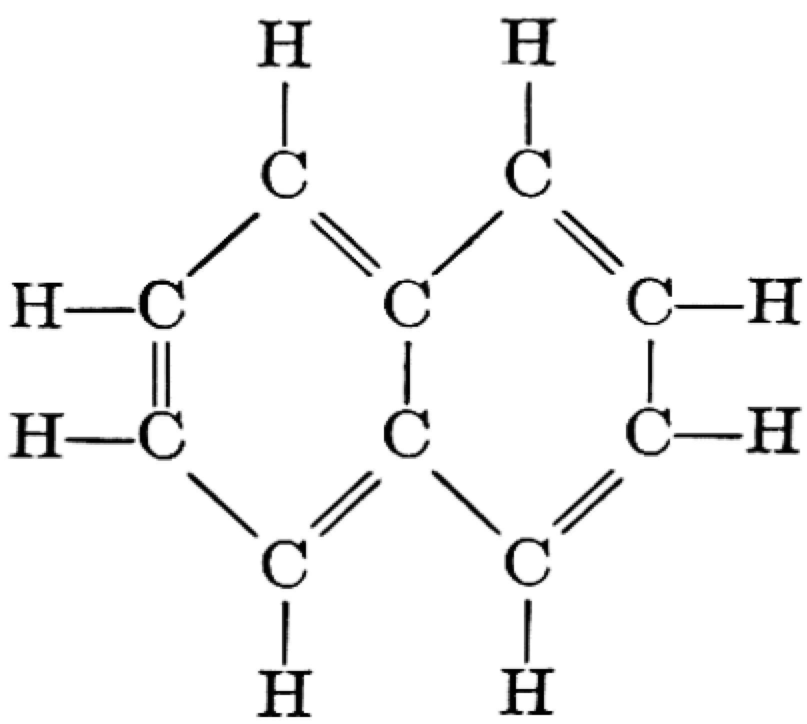
331 Condensed Benzene Nuclei

The compounds toluene and the three xylenes are combinations of the aromatic benzene nucleus with one or more aliphatic radicals

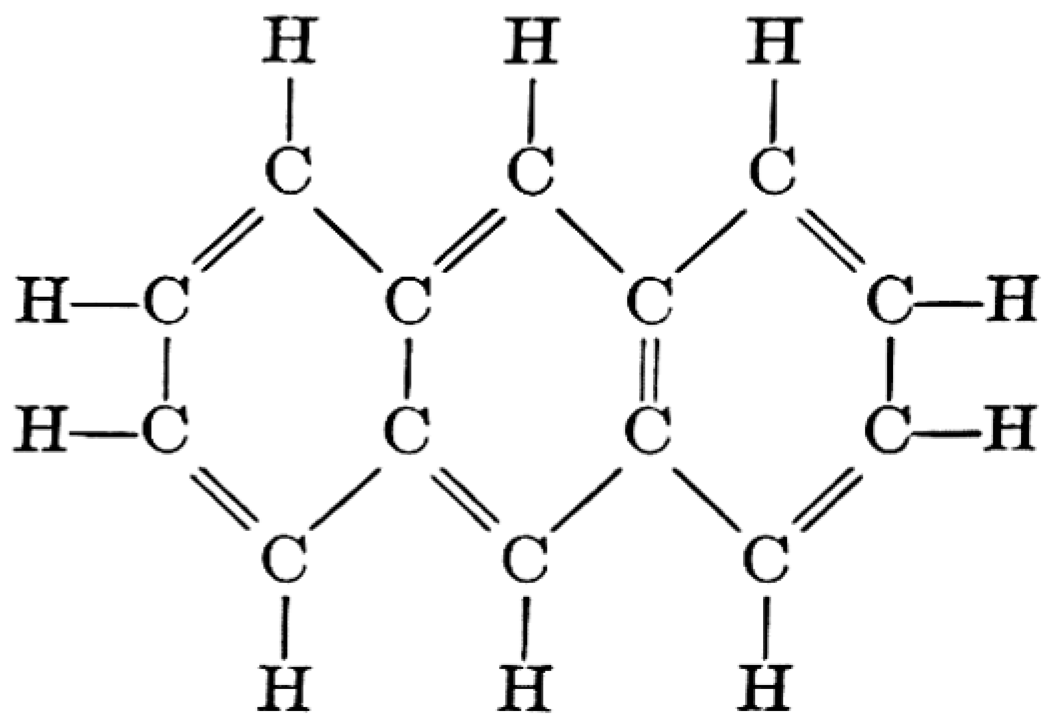
joined thereto. In the following example it is seen that two benzene nuclei can themselves be joined together, forming diphenyl, $C_6H_5—C_6H_5$:



But naphthalene, anthracene and phenanthrene cannot be regarded as homologues of benzene; rather are they condensed benzene nuclei:

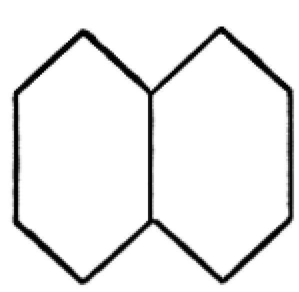


Naphthalene
($C_{10}H_8$)

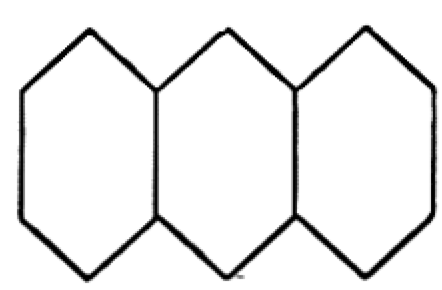


Anthracene
($C_{14}H_{10}$)

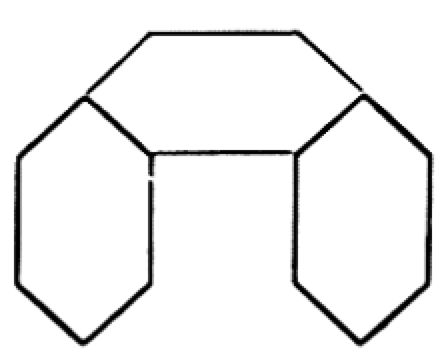
Isomeric with anthracene is the hydrocarbon phenanthrene. All three compounds are usually represented in the hexagonal manner thus:



Naphthalene



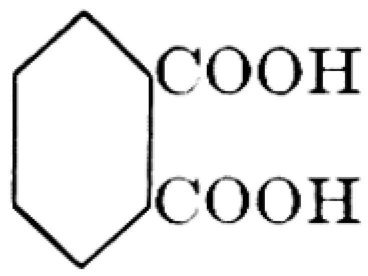
Anthracene



Phenanthrene

Substituents of these compounds produce isomers analogous to those found with benzene, except that here the isomerism is much greater. Naphthalene and anthracene give rise to many synthetic substances besides occurring combined in many natural products.

An important product of naphthalene is obtained by oxidation, which splits off two carbon atoms and leaves a dicarboxylic acid, *o*-phthalic acid, $C_6H_4(COOH)_2$.



o-Phthalic acid

332 Summary

Cyclic is the general term used to describe compounds whose properties and reactions are best expressed by arranging the component atoms in the form of a ring. If the atoms composing the ring are all alike (for example, cyclohexane), the compound containing them is called homocyclic; if the atoms are unlike, the compound is heterocyclic (examples in Chapter 23).

A ring of fewer than five atoms is generally unstable, that is, the compound so formulated tends to be unstable. The analogy is found in a ring of tetrahedra, which has less strain in it if five are linked together than if three or four are so linked.

Paraffin hydrocarbons may be treated to give a ring compound such as cyclohexane—one of the cycloparaffins, so-called. These cycloparaffins have their alcohols, aldehydes, etc., just as the paraffins, olefines and acetylenes.

The cycloparaffins may be regarded as intermediate between the aliphatic chain compounds and the cyclic compounds, of which benzene (C_6H_6) is the first and simplest. The two main divisions of carbon compounds are therefore aliphatic and aromatic.

Benzene is an excellent example of aromatic compounds. It appears to possess double bonds, but they are not of the nature of those found in ethylene. Benzene and its homologues seldom suffer addition; they are substituted.

Substituting in the benzene ring (or nucleus) is simply demonstrated by using a hexagon to represent the C_6H_6. Substitution by more than one radical produces isomerism; for two substituents, three isomers; for three substituents, three isomers.

Benzene and sulfuric acid produce benzene sulfonic acid ($C_6H_5SHO_3$); with nitric acid nitrobenzene is obtained ($C_6H_5NO_2$).

With more than one substituent their positions around the ring must be indicated, either by letters (*o*, *m*, *p*, etc.) or by numerals.

Toluene ($C_6H_5 \cdot CH_3$) is both aromatic (possessing the benzene ring) and aliphatic because of the side chain, the methyl radical. It can behave, therefore, as if it were both benzene and methane (within limits).

Groups of rings based on the benzene nucleus—condensed benzene nuclei—show reactions similar to those of benzene but of much greater isomerism. Examples are naphthalene, anthracene, phenanthrene.

The industrial importance of aromatic compounds lies in the great variety of explosives, medicinals and dyes whose constitutions are based on benzene.

Questions

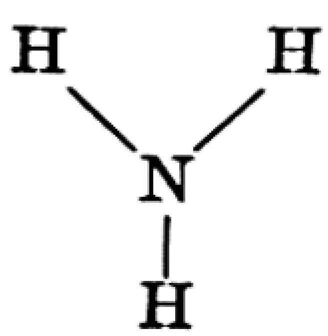
1. Compare the graphical formulae of cyclohexane, benzene, *n*-hexane.
2. Show graphically what occurs when benzene is treated with (*a*) bromine, (*b*) nitric acid and (*c*) sulfuric acid. Name the product in each instance.
3. Using regular hexagons, draw the formulae of benzene, phenol, aniline, diphenyl, naphthalene and anthracene.

23

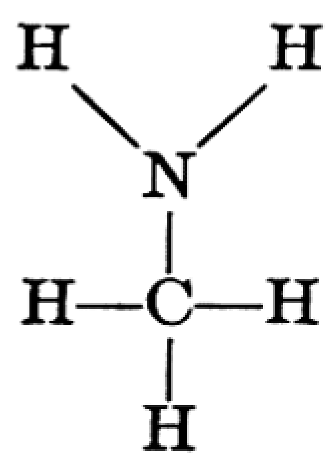
Organic Nitrogen

333 The Amine Type

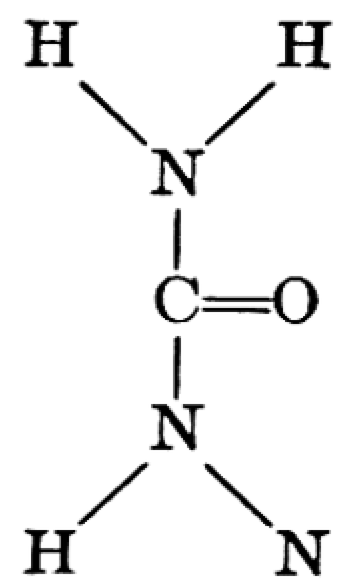
Two important nitrogen groups attached to carbon have already been referred to as amines (§ 284) and nitro compounds (§ 328). The latter are of interest chiefly when associated with benzene or other aromatic substances. But amines compose a larger part of the very important study of combined nitrogen, more particularly since it is in the form of amine-like compounds, of which the fleshy structure of animals is built up and maintained. The graphical formula for ammonia, which is the basis of all amino compounds, contains three hydrogen atoms, of which one or all may be replaced. Some characteristic examples are:



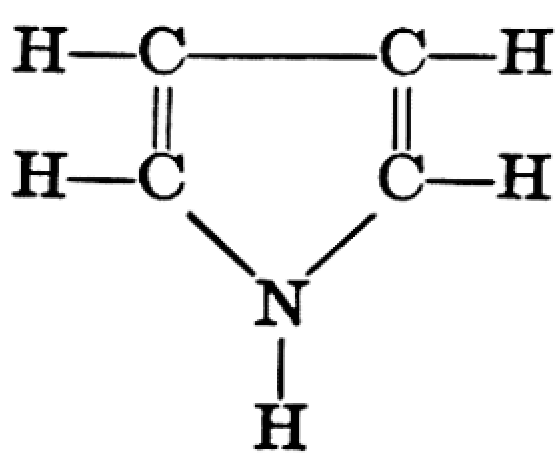
I



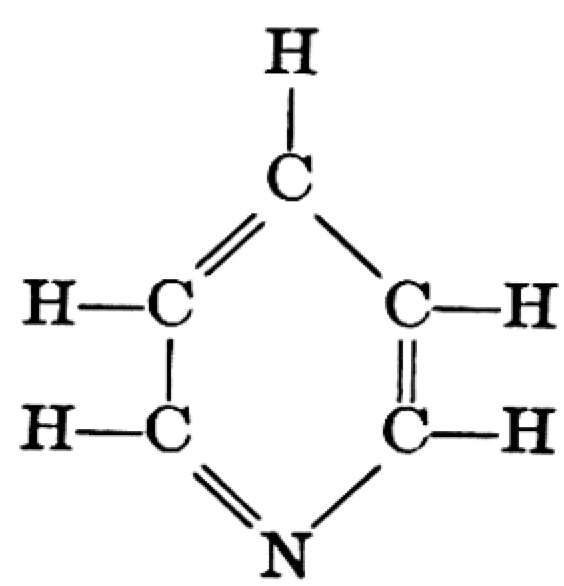
II



III

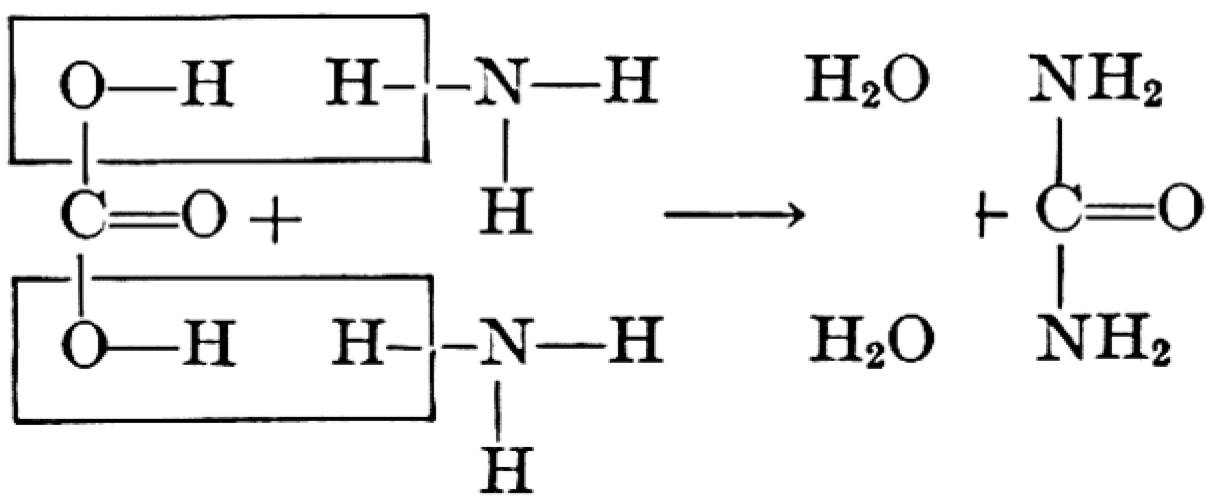


IV



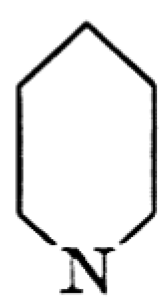
V

I represents ammonia, whose properties have been described previously (§ 65). II is methylamine, a compound of ammonia in which one hydrogen of ammonia has been replaced by the methyl radical. III is a urea, a common constituent of all animal urine, and hence the chief decomposition product of animal tissues. Its relationship to ammonia and to carbonic acid appears from this equation:



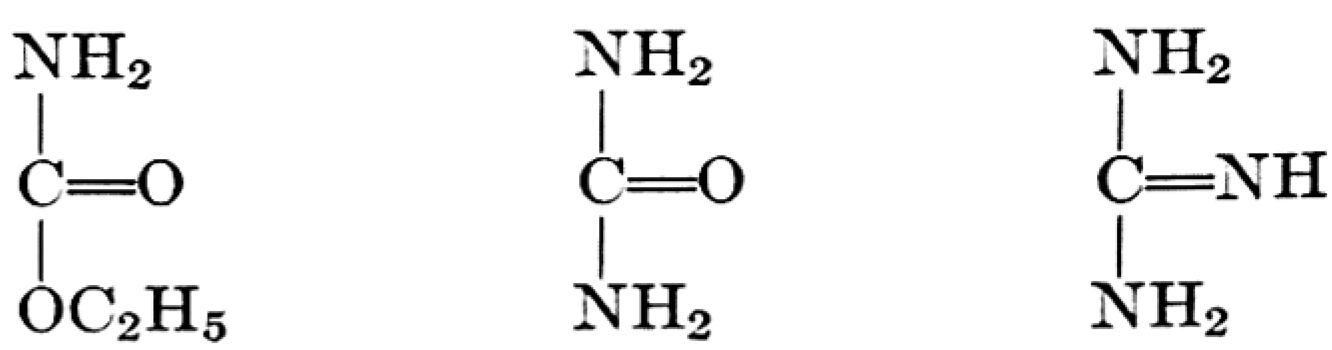
(130)

where two molecules of ammonia are shown, each releasing one hydrogen atom to form a molecule of water with each of the two hydroxyl radicals of carbonic acid, and to produce the new compound urea. IV is pyrrole, a carbon-nitrogen complex found in certain important cell structures, and V is pyridine; the latter is found in a large number of alkaloids and is frequently represented by a split hexagon reminiscent of benzene.



334 The Ureas

Closely related to urea are urethane and guanidine:

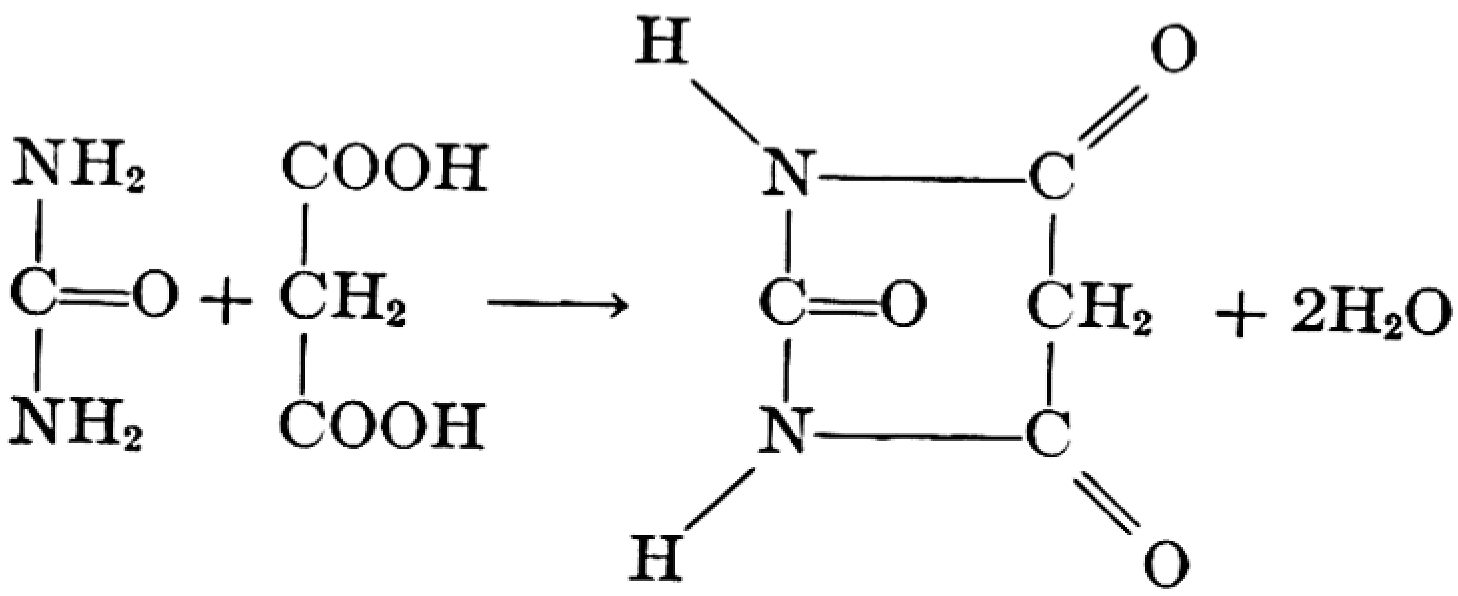


Urethane Urea Guanidine

Guanidine is a constituent of guano, the excreta of birds, which was once so important a fertilizer that a regular sea-borne trade existed to transport it to Europe from the islands of the south Atlantic. Urethane is a representative of a group of substances in which a variation of the ethyl radical produces useful soporifics (sleep-producers).

335 The Ureides

When urea is combined with dibasic or dicarboxylic acids it gives rise to a series of compounds known as ureides; for example, with an acid called malonic it gives barbituric acid, or malonyl ureide:

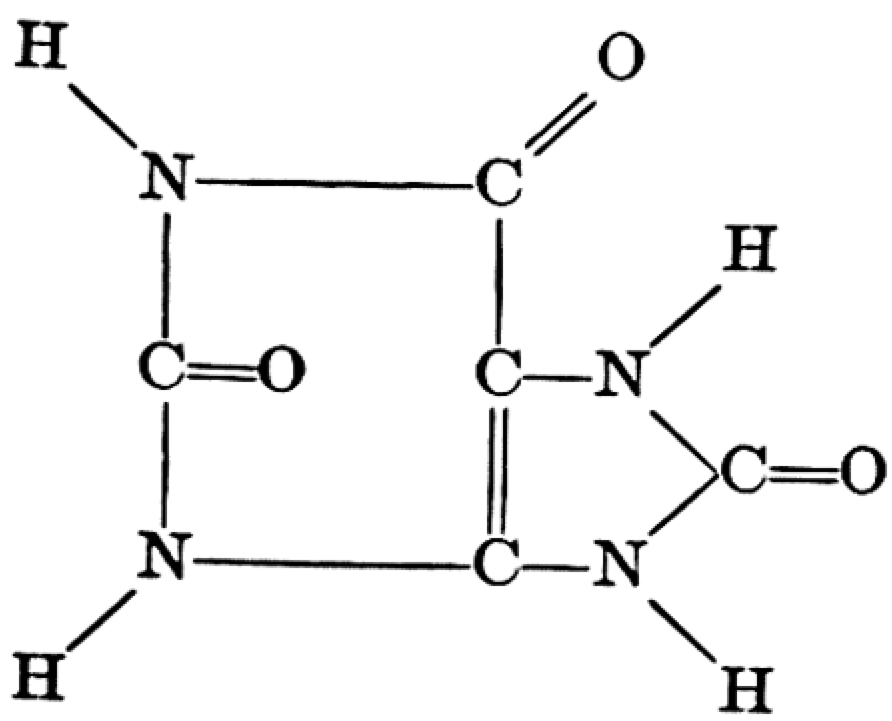


Urea Malonic acid Barbituric acid (131)

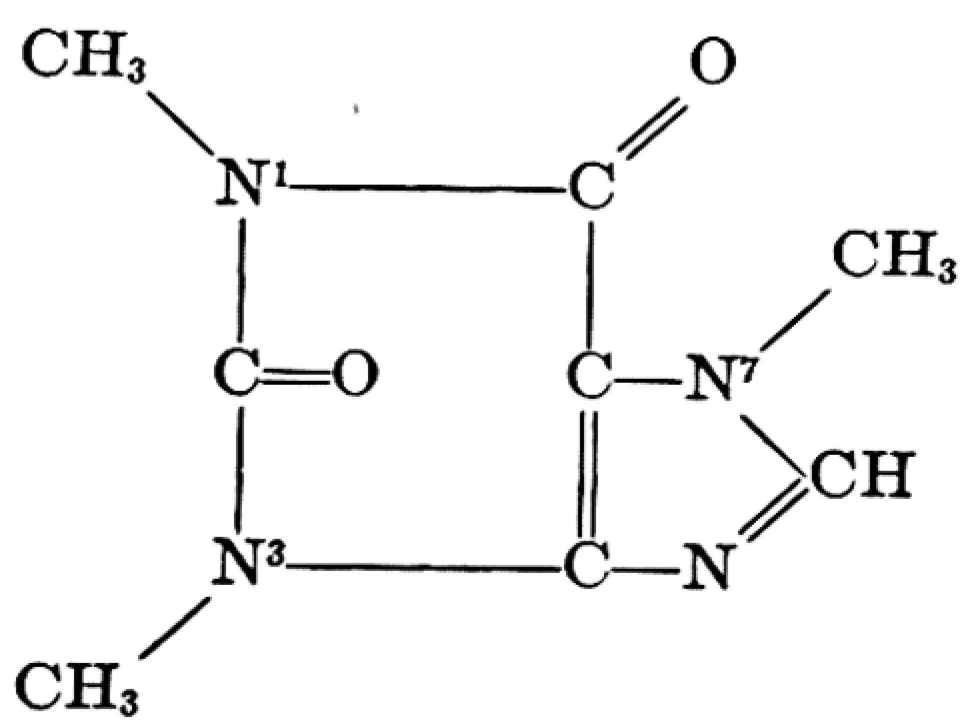
This compound is of no special importance by itself. If, however, the hydrogen atoms of the —CH_2— grouping are replaced by ethyl, propyl, butyl, amyl and phenyl radicals, the derivatives so produced (substituted ureides) are of considerable medicinal value.

336 Pseudoalkaloids

Closely related to urea and barbituric acid is a large number of compounds known as the purines, which form an important part of the nitrogenous content of living cells. Derived from them are many compounds of importance in our daily life, such as uric acid, caffeine and related compounds.



Uric acid



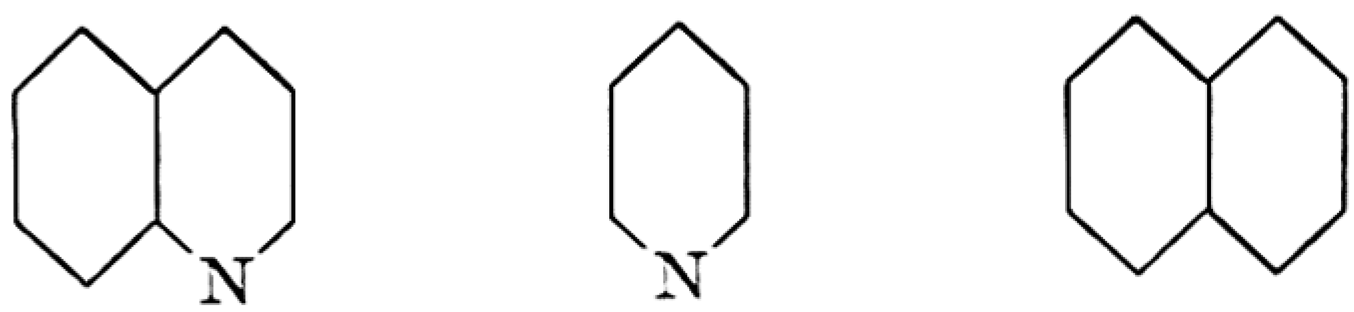
Caffeine

Uric acid may be regarded as two urea molecules condensed with one of malonic acid, that is, a barbituric acid derivative. It is a decomposition product of animal muscle tissue. Caffeine is simi-

larly related to both barbituric acid and uric acid with methyl groups in the 1, 3, 7 positions. Theobromine is caffeine with CH_3— in 1 replaced by hydrogen; theophylline is caffeine lacking the CH_3— in 7 and with a hydrogen atom in its place. These compounds, caffeine (or theine), theobromine and theophylline, are sometimes called pseudoalkaloids. They may be found in such beverages as tea, coffee, and chocolate.

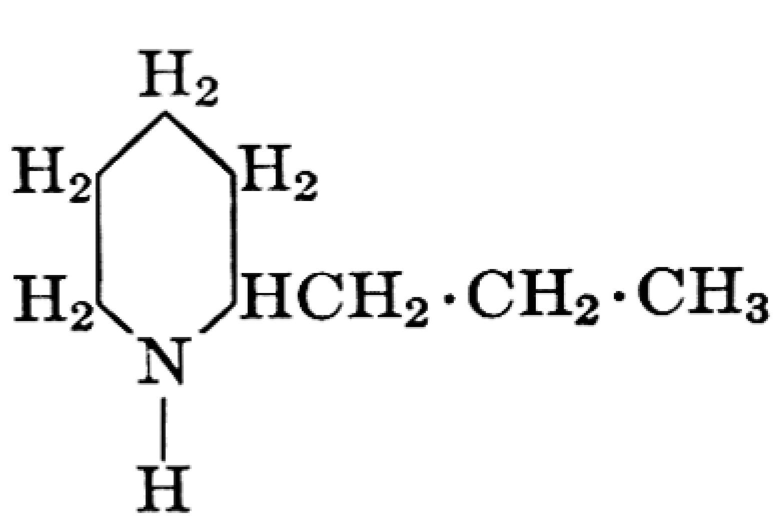
337 Alkaloids

When condensed with a molecule of benzene, pyridine gives quinoline which bears a structural resemblance to naphthalene:



Quinoline Pyridine Naphthalene

Pyridine and quinoline are essential to the structure of such alkaloids as coniine, the poisonous constituent of hemlock, nicotine, the principal alkaloid of tobacco and many others. The formulae of coniine and nicotine are given below for illustrative purposes:



Coniine Nicotine

Alkaloids are products of plant life commonly found in the stems, leaves and bark. They are usually insoluble in water, but may add on acids (as does ammonia) to form soluble salts. It is this property which gives rise to their general name. Several such, as quinine, morphine, atropine and heroin, are used medicinally.

338 Proteins

Of greater importance than the amino compounds so far mentioned is that complex aggregation of nitrogenous matter known as the proteins. They are large molecular aggregations, to whose

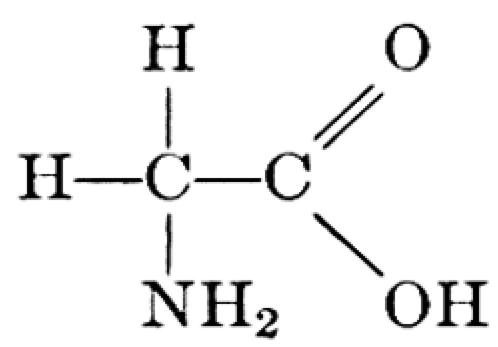
structure it is difficult to assign any arrangement; they show the behavior of colloids. What we know of their make-up has been discovered by hydrolysis, in this case boiling various animal and vegetable tissues in water containing a strong acid or alkali. Gradually the protein (such as wool, hair, muscle tissue) disintegrates and dissolves, giving rise to relatively simple products, all of which contain carbon, hydrogen, oxygen and nitrogen, and some of them sulfur as well. But the element that sets the proteins apart as essential to organic life is the nitrogen they contain; for they are derivatives of ammonia, where the amine group ($—NH_2$) appears in each of the amino acids listed. The process of hydrolysis of the complex protein to the simple end products, the amino acids, is indicated according to this scheme:

Proteins → proteoses → peptones → polypeptides → amino acids

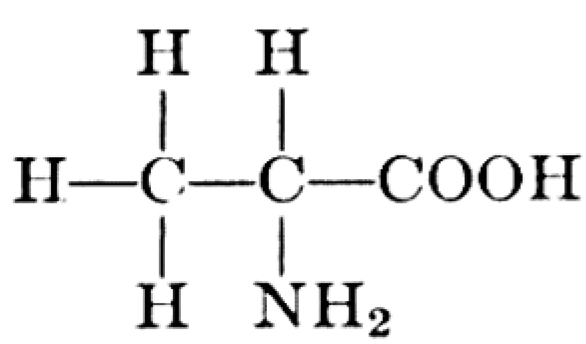
The proteins are amides.

339 Amino Acids

The simplest amino acid is amino acetic acid, also called glycine and glycocoll. Its formula shows both the carboxyl radical



($—COOH$), indicative of acid properties, and the amino radical ($—NH_2$), which possesses basic properties; thus the molecule of glycine can display both sets of properties. An amino acid much more commonly found in protein hydrolysis is alanine, or alpha amino propionic acid; alpha amino because the $—NH_2$ is attached

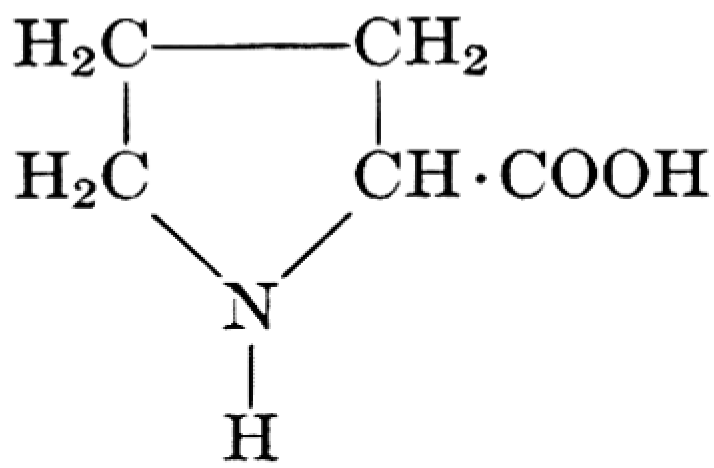


to that carbon atom which is next to the COOH. This amino acid typifies the others, which contain a larger number of carbon atoms, since all amino acids contain one amino radical on the alpha carbon atom. The names and formulae of other well-known amino acids are given here merely to indicate certain similarities

and dissimilarities of structure:

Leucine $(CH_3)_2CH \cdot CH_2 \cdot CHNH_2 \cdot COOH$

Proline



Glutamic acid $HOOC \cdot CH_2 \cdot CH_2 \cdot CHNH_2 \cdot COOH$

Cystine

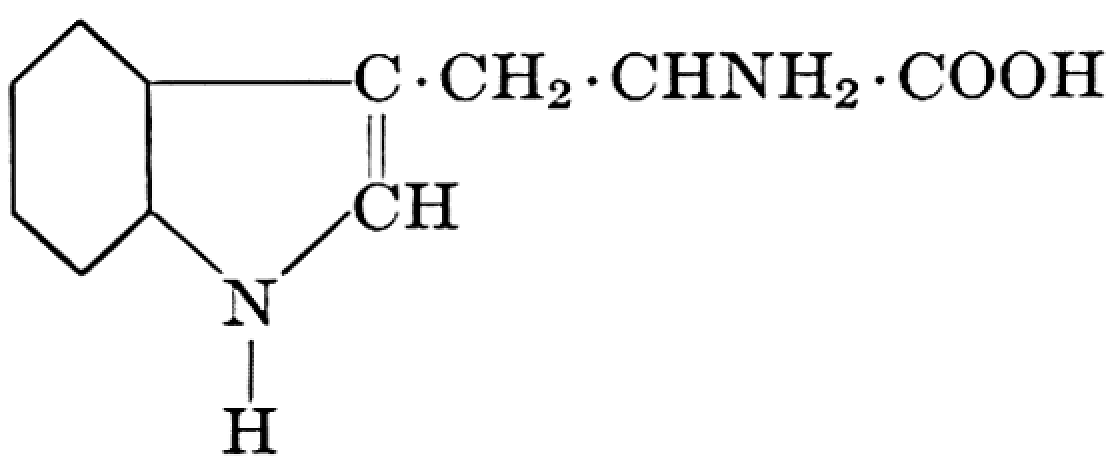
$$\begin{array}{l} S \cdot CH_2 \cdot CHNH_2 \cdot COOH \\ | \\ S \cdot CH_2 \cdot CHNH_2 \cdot COOH \end{array}$$

Arginine

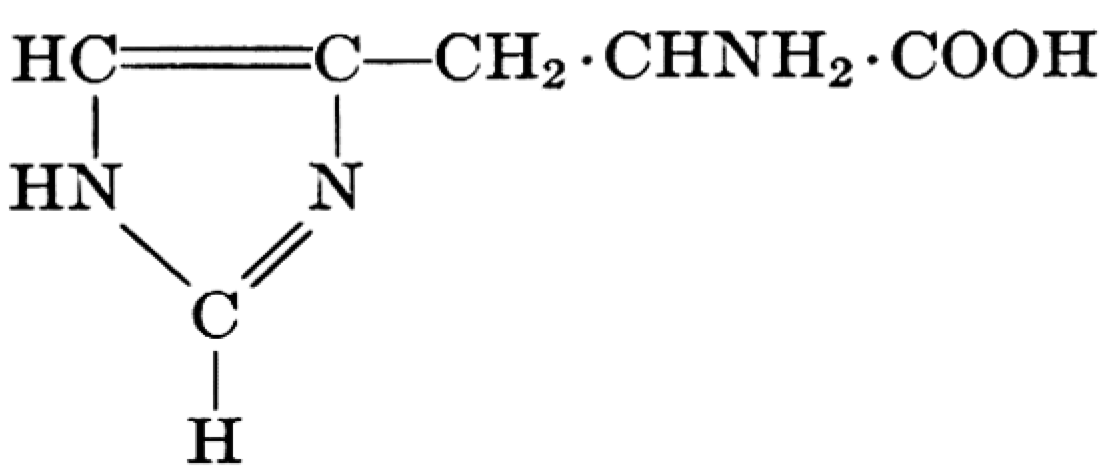
$$\begin{array}{l} NH_2 \\ | \\ C\text{—}NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHNH_2 \cdot COOH \\ \| \\ NH \end{array}$$

Lysine $NH_2CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHNH_2 \cdot COOH$

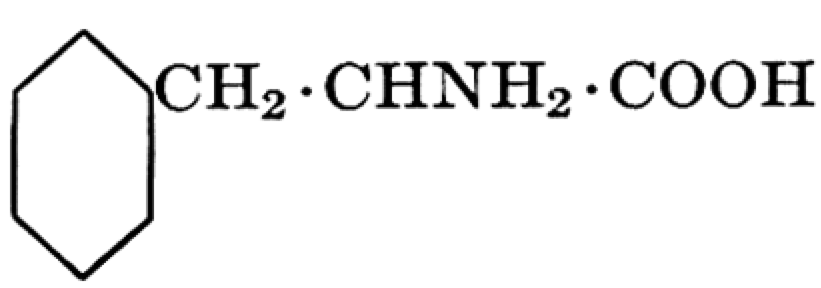
Tryptophane



Histidine



Phenylalanine



Of these the one found in greatest degree is glutamic acid.

An attempt was made by Emil Fischer, whose contribution to carbohydrate chemistry is so well known, to elucidate the structure of the proteins by synthesis. He was not completely successful,

but he did manage to link together twenty-two amino acid units into a compound closely resembling the peptones, which are very simple proteins. Recently greater success has been achieved.

340 Nuclear Proteins

Living cells contain relatively small nuclei composed of proteins more or less characteristic of the species of plant or animal to which they belong. This is to be expected since a nucleus is the source from which arises the new life of the cell with all its inherent characteristics. The proteins of cell nuclei are usually phosphates, in which phosphoric acid is linked up with a carbohydrate and several amino acids; hence the term nucleic acids for these complexes. Though all such nucleic acids differ among themselves, there is a broad classification possible into two types, vegetable and animal.

The chief sources of proteins are the grains, the muscle tissue of fish and land animals, eggs and milk. Not all proteins are of equal value as foods, since feeding experiments have demonstrated the necessity of a grouping of amino acids to the growth and maintenance of life.

Casein, the protein of milk, has considerable industrial value also since it may be converted into a hard, insoluble, resin-like solid capable of being molded into a variety of useful articles.

341 Summary

The element nitrogen occurs in a minority of carbon compounds, but these compounds are of great significance in life processes. It is always as derivatives of ammonia that combined nitrogen is found, that is, of the amino type.

Urea is a derivative of carbonic acid and ammonia and is of the chain type of structure. But, condensed with a dibasic acid—one containing two carboxyl groups (—COOH)—such as malonic acid, urea forms a ureide of the acid, for example, malonic ureide or barbituric acid. This is a heterocyclic compound.

Derivatives of barbituric acid are used as medicines.

Barbituric acid has a structure on which may be built the compounds occurring in both animals and plants. Examples are uric acid and the pseudo-alkaloids, caffeine, theobromine.

In both kingdoms of living matter a second type of compounds, amino acids, occurs. They are similar to the paraffin-derived acids in having usually one —COOH radical; but in addition they carry an amino (—NH_2) radical on the carbon atom next to the carboxyl. Hence they are known as alpha amino acids. These acids may be obtained by the progressive hydrolysis of the large colloidal aggregations known as proteins. As these amino acids are definitely

units of living cells, they are essential to the growth and maintenance of living matter.

An amino acid is balanced in its activity between an alkali and an acid—hence amphoteric. A pyridine derivative is alkaline, as is ammonia, and can therefore add acids just as ammonia does.

A third type of nitrogen compounds resembles benzene except that one —CH— of benzene is replaced by a nitrogen atom. Pyridine is a good example of this type. All naturally occurring alkaloids (as nicotine and quinine) contain this structure.

Questions

1. Write graphical formulae for benzene, pyridine, naphthalene and quinoline.
2. What is a ureide? What importance attaches to barbituric acid?
3. What essential difference is there between alkaloids and pseudoalkaloids? How is caffeine related to uric acid?
4. What general similarities are to be found in the formulae of amino acids?
5. How are proteins related to amino acids?

24

The Carbohydrates

342 Nomenclature

The name carbohydrate was intended to suggest a compound whose components are carbon, hydrogen and oxygen, the last two present in the proportion in which they exist in water, that is, two to one. Though this ratio is not maintained throughout, it is so generally found that the name carbohydrate has become incorporated in chemical nomenclature to designate a definite class of substances, some simple, some complex, but all closely related. This atomic relationship is exemplified by $C_6H_{12}O_6$, $C_6H_{10}O_5$ and $C_{12}H_{22}O_{11}$—all the empirical formulae we are concerned with here. This class of compounds is treated here separately, not because of their chemical and structural relationships but by virtue of their necessity as energy-producing foods and their very wide application in the industrial arts. And though many members of this class are known, our concern is with those which, occurring naturally, are therefore the raw materials for our biological and industrial consumption.

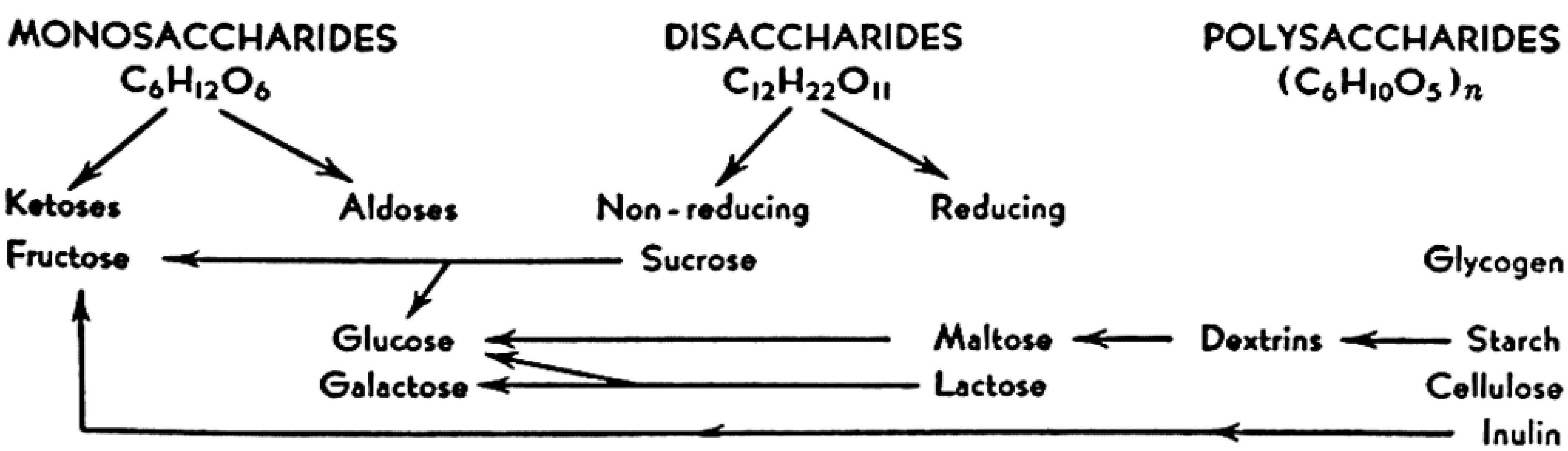


FIG. 67. Hydrolytic relationships of some carbohydrates.

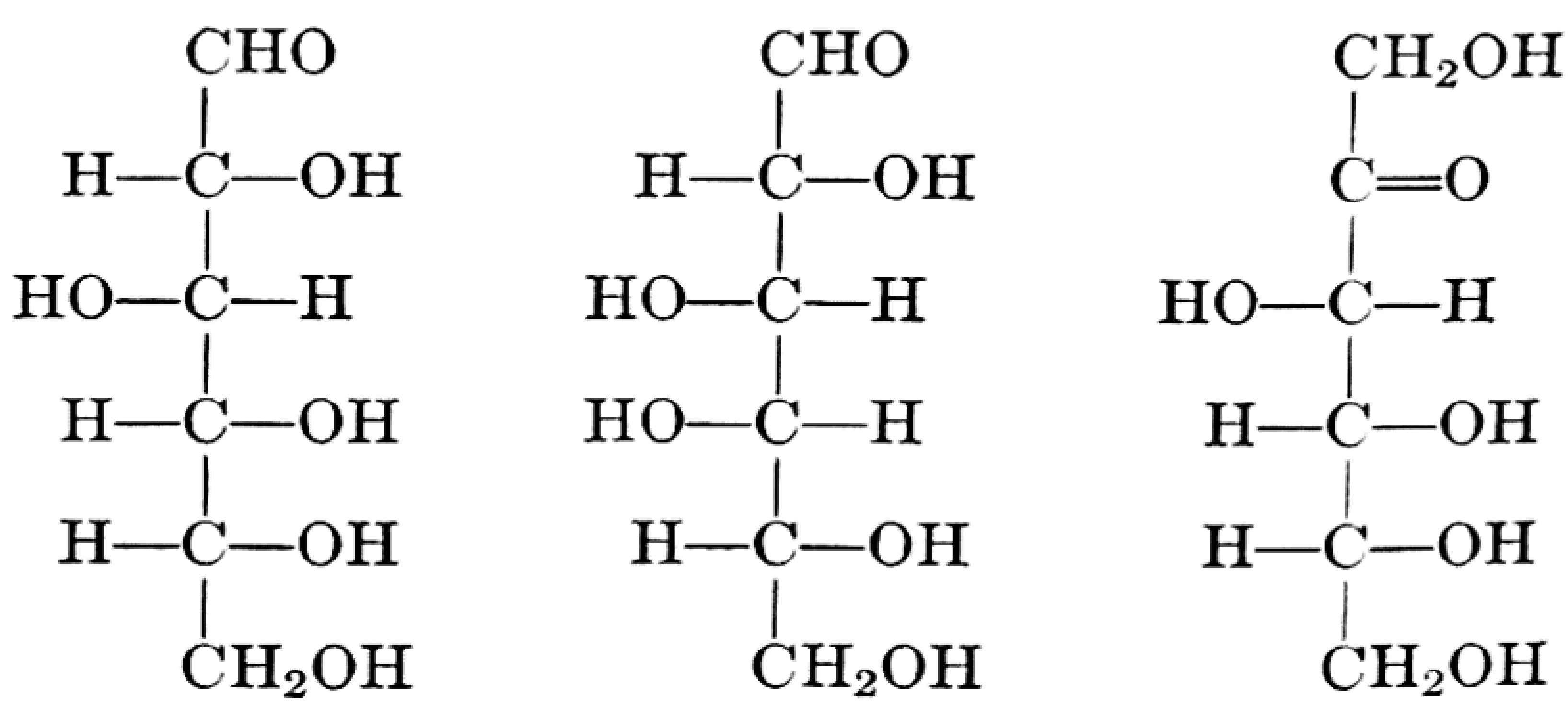
343 Classification

The carbohydrates may be most conveniently classified as monosaccharides, disaccharides and polysaccharides, of respective

empirical formulae $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$ and $(C_6H_{10}O_5)_n$. (See Fig. 67.)

344 Monosaccharides

Many monosaccharides can be shown to possess in solution five hydroxyl groups and either an aldehyde group (—CHO) or a ketone group $\left(>C=O \right)$. The aldehyde monosaccharides are termed aldoses, and the ketone variety ketoses, the termination *ose* being a modern one to designate a carbohydrate wherever possible. Since these monosaccharides contain six carbon atoms to the molecule, they are called hexoses. Two examples of hexose aldoses are glucose (also called dextrose or grape sugar) and galactose (so named from its relation to lactose or sugar of milk, a disaccharide). Both glucose and galactose can react to give the silver-mirror test for aldehydes (§ 285); hence they are also known as reducing sugars.[1] A familiar example of a ketose is fructose, also known as levulose (as opposed to dextrose) or fruit sugar. Below are the simple formulae which may be used to illustrate the differences in the structure of these three hexoses:



Glucose Galactose Fructose

A study of these formulae will show that all three possess the same numbers of similar atoms; they are thus isomers. In addition, however, between glucose and galactose there is only the difference of the relative positions of the H and OH on the two middle carbon atoms.

[1] So as not to confuse the terms carbohydrate and sugar, sugar may be regarded as a particular type of carbohydrate, being soluble in water and sweet to the taste. Some other carbohydrates are neither.

345 Glucose, Fructose, Galactose

Glucose or grape sugar is found in grapes, as might be supposed; but, like fructose, it is found in many other ripe fruits also. Both are sweet and occur together in considerable amount in honey. Glucose may be produced by the hydrolysis of both cane sugar and starch, and when prepared from starch is a cheap and useful sweetening substance. Galactose is obtainable only by the hydrolysis of lactose, which, in turn, occurs only in the milk of mammals. It is not fermentable, as are glucose and fructose, to produce ethyl alcohol, but produces lactic acid, the acidic constituent of sour milk. The fermentation of glucose to produce ethyl alcohol is of considerable importance industrially (§ 497).

346 The Disaccharides

The disaccharides have the formula $C_{12}H_{22}O_{11}$ and may be seen to be made up theoretically of two monosaccharide molecules less a molecule of water, though this has never yet been achieved practically. Thus the equation

$$2C_6H_{12}O_6 - H_2O \rightarrow C_{12}H_{22}O_{11} \qquad (132)$$

suggests the term disaccharide, since the number of carbon atoms has doubled. The reverse process is easily feasible, however, for, by being warmed in water with a few drops of hydrochloric acid, a molecule of $C_{12}H_{22}O_{11}$ will add the elements of water to produce two $C_6H_{12}O_6$ molecules; this is another case of hydrolysis.

347 Lactose, Maltose, Sucrose

The disaccharides may be subdivided into two classes, *reducing* and *non-reducing* sugars, for the same reason as the monosaccharides. Maltose, or malt sugar, and lactose, or milk sugar, are examples of reducing disaccharides, whereas cane sugar, or sucrose, is non-reducing. Maltose, a slightly sweet sugar, is produced during the moist fermentation of barley. Lactose occurs to the extent of about 3 per cent in cow's milk, where on fermentation it changes to lactic acid, which renders the milk sour; it is only very slightly sweet. Sucrose is produced in large quantities by the sugar cane, the sugar beet, the maple tree and many other plants. Its usefulness depends on its intense sweetness.

The reducing disaccharides are those which, like the aldohexoses, are capable of showing their possession of an aldehyde group in

aqueous solution; hence they give the silver-mirror test. On the other hand, sucrose does not demonstrate this property and is therefore termed non-reducing. If the aqueous solution of these sugars is heated with a little of a strong acid such as hydrochloric, the disaccharide molecule picks up the elements of water to hydrolyze into two molecules of monosaccharide. Empirically this is shown as follows:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \tag{133}$$

Thus maltose yields two molecules of glucose, lactose one molecule of glucose and one of galactose, and sucrose one molecule of glucose and one of fructose; the mixture of glucose and fructose is known as invert sugar. These relationships are shown diagrammatically in Fig. 67.

348 The Polysaccharides

They are given the formula $(C_6H_{10}O_5)_n$, the significance of which is that analysis has determined the proportions of the three elements present but that molecular weight measurements do not indicate actually how many such units make up the molecule. The unit itself would appear to be the equivalent of a hexose which has lost two atoms of hydrogen and one of oxygen. These polysaccharides are relatively insoluble in water, though on hydrolysis with dilute acids they readily break down with addition of water molecules to the hexoses (Fig. 67). Cellulose, the backbone of plants, is a fibrous structure which enjoys great industrial application (Chapter 34); starch is the white, amorphous food reserve of plants; inulin is found in certain mosses; and glycogen, the reserve energy compound of animals, is a white solid slightly soluble in water.

In the plant kingdom all the polysaccharides and disaccharides are synthesized from carbon dioxide and water in a manner which has never been reproduced in vitro. Emil Fischer, whose carbohydrate researches are classical, succeeded in synthesizing a saccharide of eleven carbon atoms from formaldehyde, but he was unable to produce the C_{12} compounds. Our knowledge, therefore, of the higher carbohydrates has been obtained by hydrolysis, which results in their degradation to the hexoses. We may illustrate this, beginning with starch.

349 Dextrinization

If a little starch is mixed into a paste with a little cold water and added to a larger quantity of boiling water, it gives rise to an opalescent liquid, while continued boiling renders the starch more soluble. The original starch paste will turn an iodine solution a deep blue in color; while boiling proceeds, the liquid, on being tested with iodine, shows a fading of this blue to a light purple. This boiling of starch gives rise to simpler products known as the dextrins; it is called *dextrinization*. When a little acid, such as hydrochloric, is added, the dextrins, on continued boiling, are degraded rapidly to maltose (which gives no color change with iodine) and thence to glucose where hydrolysis ends. This entire process from beginning to end may be represented as follows:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad (134)$$

Glycogen and cellulose on similar hydrolysis also yield the aldose glucose, and inulin yields fructose, a ketose.

350 Cellulose

This is the chief component of plant fibers, cotton being its purest natural form; from the stalk of the flax plant linen is obtained, and from certain soft woods, wood pulp. They are the most useful forms of cellulose, the first two being used largely in woven articles. Ground wood pulp is now used by the thousands of tons annually in the manufacture of paper. The pulp for this purpose may be prepared either by mechanical or by chemical means. In the manufacture of paper, treated wood pulp is washed, dried and rolled. Various quantities of rags are incorporated with it, depending on the grade of paper required. A filler, such as barium sulfate or zinc oxide, and rosin for sizing are then added.

Artificial silk is a general term used to describe a variety of products prepared by treatment of cellulose (either cotton or wood pulp). It has, to a great extent, replaced natural silk, which is a product of the silkworm. In no sense is it silk, a protein of animal origin; rather it is a derivative of the carbohydrate cellulose, that is, it is a substitute for silk though in many respects it may be preferable to silk. These products are listed under such names as mercerized cotton, Viscose silk, nitro silk and Celanese, and their preparation is described later (Chapter 34).

351 Light and Isomerism

Certain classes of carbon compounds display a type of isomerism which is related to their action on light. It has been established that the optical properties of crystals are in agreement with the symmetry of the external form and that both are related to the internal arrangement of the atoms or ions in the molecule. In certain classes of crystals light does not travel with a uniform

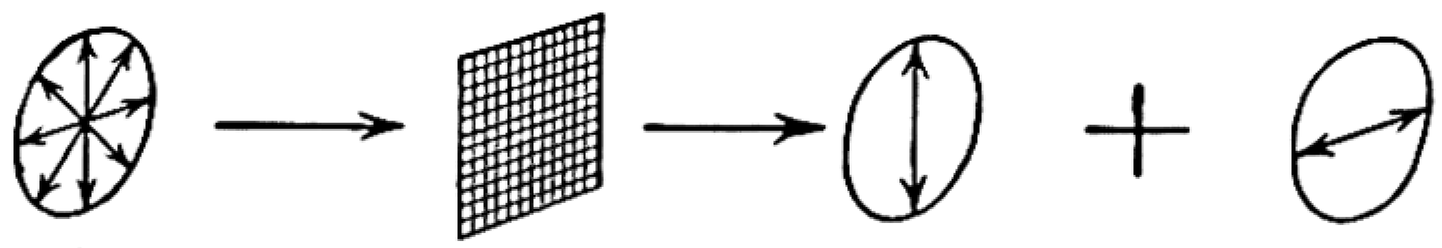


FIG. 68. Normal light can be polarized by passing through certain substances which divide the vibrations into two planes at right angles to each other.

velocity in all directions. If a beam of light is passed through a suitably chosen section of such crystals, it will be broken up into two beams of different velocities. Then the incident beam may be considered as composed of vibrations in all directions at right angles to the line of propagation (Fig. 68). However, on emerging from the crystal it is plane-polarized in two beams at right angles to each other, and in each beam the light waves, instead of vibrating in all directions at right angles to the line of travel, now vibrate in one plane only. With some naturally occurring substances one of the emerging beams is completely absorbed, leaving only one to be transmitted. A Nicol prism is a device for producing the same result. In addition, some substances with an internal structure resembling a corkscrew can cause the plane of polarization to be rotated; such substances are said to be optically active.

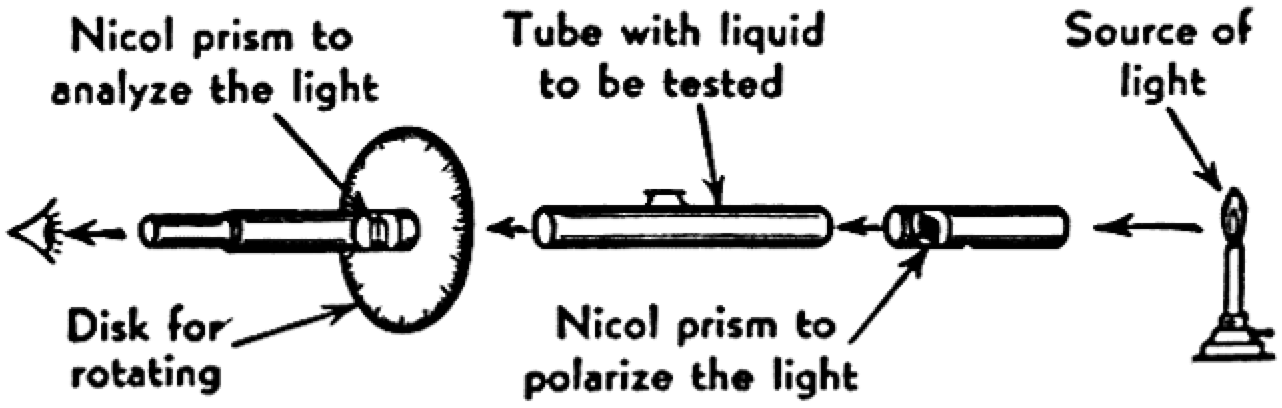


FIG. 69. Essentials of a polariscope reading.

352 Optical Rotation

An instrument known as a polariscope (Fig. 69) is used to detect and measure such optical activity. A beam of light enters a Nicol prism, emerging polarized in one plane. It then passes through a solution (aqueous preferably) of the substance suspected of optical

activity; thence it passes to another Nicol prism and finally to the eye of the observer. To accomplish this, the two Nicol prisms and the solution must be in such alignment as to permit the beam of light to get through; for if the solution rotated it, the second Nicol would itself need rotating. The angle through which the second Nicol needs rotating and the direction (right or left) determine the optical activity of the dissolved substance. If rotation to the right is necessary, the solute is called *dextrorotatory;* if to the left, *levorotatory.*

353 Asymmetry

It has been found that organic substances capable of causing such rotation show in their internal structure the existence of four different groups attached to the one carbon atom, this atom being called asymmetric for that reason. A simple example of such a compound is lactic acid where the central carbon atom has the four different groups CH_3, H, OH and COOH. It may be represented in two dimensions as follows:

The lactic acids

We know of the existence of two distinct lactic acids whose chemical properties are similar but differ chiefly in this one light property.

If the solution of lactic acid requires rotation of this disk to the observer's right to permit emergence of the beam of polarized light, the solution in the tube is called dextrorotatory; if to the left, it is called levorotatory. These two forms are then termed *optically active* and are said to be *optical isomers,* whereas a mixture of both in equal proportions will have their rotations balanced. Such a mixture is said to be *racemic* and optically inactive. Such relationships as the above are best represented by actual space models.

354 Tartaric Acid

In the middle of the last century Pasteur, the great French bacteriologist, studied the tartaric acids (of which there are four) and elucidated their structural differences. He found that

two of them, which were optically active, crystallized (as salts) from solutions in two forms, showing that they were enantiomorphic, that is, the crystals of one form differed from those of the other form as the right hand differs from the left in being similar but not superimposable. These crystalline differences were found to have their counterpart in the action of each on polarized light.

355 The Sugars

This light property is found in most carbon compounds which are associated with life. Thus the glucose which occurs in nature is found to be dextrorotatory, and levorotatory glucose must be prepared synthetically. In the same way fructose occurs in its levorotatory form; hence the former names dextrose and levulose for these two sugars. Cane sugar is slightly dextrorotatory, but the mixture of hexoses to which it gives rise, namely, glucose and fructose, is slightly levorotatory. This mixture is termed *invert sugar* because of the change of rotation (*inversion*) which occurs on hydrolysis. Thus each optical isomer has its counterpart, but in nature the general rule is that only one form is delegated to some particular function, no matter how similar their other properties may be. Where both forms are known to occur they are likely to result from the exercise of quite different functions. For example, the lactic acid which results from the fermentation of lactose in milk is levorotatory, whereas that found in muscle tissue is dextrorotatory and is called sarcolactic acid.

356 Life and Optical Activity

The interrelation of optical activity in carbon compounds and the processes of living organisms (themselves complexities of carbon) is seen in the following examples.

If a mixture of the dextrorotatory and levorotatory forms of tartaric acid is subjected to the action of a certain fungus, the fungus feeds on and decomposes the dextro acid, a naturally occurring product found in grape juice, but does not attack the synthetically prepared levorotatory acid. Similarly, if a mixture of the two glucoses is treated with yeast, it is the natural dextro variety which is fermented to form ethyl alcohol and carbon dioxide and not the artificially prepared levo compound. Thus it would appear that only certain optical forms can be utilized by living organisms. A further example is seen in adrenaline, a drug

which in small quantities causes contraction of the arteries. This substance, isolated from the suprarenal glands of sheep, is levorotatory, and has more than ten times the physiological effect of the synthetically prepared dextrorotatory adrenaline. Such examples may be multiplied indefinitely, but they would serve only to confirm what has already been indicated, that vital forces are selective rather than haphazard and that there is a deep scientific chasm between an ordered and an unordered scheme of existence.

357 Summary

Carbohydrates are substances composed of carbon, hydrogen and oxygen, the last two elements being present usually in the proportion of two to one. But, since this definition includes some other compounds which are not carbohydrates, it is better to consider carbohydrates as those substances which contain several hydroxyl radicals (—OH) and either an aldehyde (—CHO) or a ketone radical $\left(> C{=}O \right)$, or a modification of these.

The modern nomenclature gives the termination *-ose* to the carbohydrates, for example, glucose, lactose, cellulose.

For convenience the carbohydrates are classified as monosaccharides, disaccharides and polysaccharides, that is, according to a unit which contains six carbon atoms. Glucose ($C_6H_{12}O_6$) is a monosaccharide; a disaccharide is sucrose ($C_{12}H_{22}O_{11}$), that is, two glucose units less H_2O; cellulose is a polysaccharide [$(C_6H_{10}O_5)_n$], that is, many glucose units less H_2O for each unit of glucose present in the molecule.

On hydrolysis (boiling in water with a little acid, for example) polysaccharides tend to pass through disaccharides and end up at the monosaccharides. Thus starch gives dextrins, then maltose (a disaccharide) and lastly glucose.

The sugars are a subdivision of carbohydrates; they are monosaccharides and disaccharides which are soluble in water and sweet. Cellulose and starch are not soluble in water, nor are they sweet.

These sugars when dissolved in water may or may not reduce ammoniacal silver nitrate to give the silver-mirror test. If they do they are known as reducing sugars or aldoses. Aldoses, like glucose, contain the aldehyde radical (—CHO) in addition to their hydroxyl radicals (—OH). If the sugar does not reduce, it is called non-reducing (for example, sucrose or cane sugar), and it does not contain the aldehyde radical. It may contain the ketone radical, however, which is non-reducing.

According to whether carbohydrates reduce or not, they are classified as aldoses and ketoses, or as reducing and non-reducing.

When polarized light is passed through a substance that contains one or more asymmetric carbon atoms, the plane of the light vibrations may be rotated to the right or left. This property of some substances is termed optical activity, and an asymmetric carbon atom is one which is attached to four different radicals.

Optical activity involves another kind of isomerism, commonly called optical isomerism. The carbohydrates exemplify this property to a high degree, but not carbohydrates only. Most life products show this property; indeed, optical activity seems to be fundamental to vital activity.

Questions

1. What is noticeable about the formula of a carbohydrate?
2. Classify the carbohydrates diagrammatically.
3. What differences are observable in the graphical formulae of glucose, galactose and fructose?
4. What are the products of fermentation of glucose and lactose?
5. Explain what is meant by hydrolysis, dextrinization, polarized light.
6. How would you distinguish experimentally between glucose and cane sugar?
7. What do you understand by the term optical activity? How is it determined?

25

Fats and Oils—Soap—Paint

FATS AND OILS

358 Glycerides

Fats are a product of all species of animal and plant life. In general the fats associated with the tissues of land animals are solid (or semi-solid) at room temperature, whereas those produced by plants and many species of fish are liquid under similar conditions. For this reason the latter variety are called oils, but there is no chemical reason to differentiate between fats and oils. Physically, then, fats may be solid or liquid. Attempts to volatilize them to the gaseous state result in decomposition with charring; they are insoluble in water, but soluble in such organic solvents as ether, benzene, carbon tetrachloride and gasoline. Chemically they are esters, and on hydrolysis give rise to the alcohol, glycerol, and acids containing a large number of carbon atoms. With rare exceptions the acids which are obtained by hydrolysis (or saponification) of these fats and oils contain an even number of carbon atoms, beginning with C_4 and continuing to C_{24} and even beyond. Thus the fat of goat's milk (from which the names of three of these acids are derived) contains the glyceryl esters, or glycerides as they are collectively termed, of C_4, C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18} saturated acids of the general formula $C_nH_{(2n+1)}COOH$. Using butyric acid as an example, we may formulate the possible synthesis of the glyceride tributyrin as follows:

$$\begin{array}{ccccccc}
\mathrm{CH_2OH} & & \mathrm{HOOC\cdot C_3H_7} & & \mathrm{CH_2OOC\cdot C_3H_7} & & \\
| & & & & | & & \\
\mathrm{CHOH} & + & \mathrm{HOOC\cdot C_3H_7} & \rightarrow & \mathrm{CHOOC\cdot C_3H_7} & + & \mathrm{3H_2O} \\
| & & & & | & & \\
\mathrm{CH_2OH} & & \mathrm{HOOC\cdot C_3H_7} & & \mathrm{CH_2OOC\cdot C_3H_7} & & \\
\text{Glycerol} & & \text{Butyric acid} & & \text{Tributyrin} & & \text{Water} \\
\text{(1 molecule)} & & \text{(3 molecules)} & & \text{(1 molecule)} & & \text{(3 molecules)}
\end{array} \qquad (135)$$

The fats have common names ending in *-in* following the name of the acid combined with glycerol, for example, palmitin, stearin.

In addition to the paraffinic acids mentioned above, there are others which are related to the ethylenes. They possess one or more pairs of doubly bound carbon atoms, and hence lack one or more molecules of hydrogen by comparison with the paraffinic acids. Examples of them are shown in Table 37. They combine

TABLE 37

COMMON UNSATURATED ACIDS

Name	*Formula*	*No. of Double Bonds*
Oleic acid	$C_{17}H_{33}COOH$	1
Linoleic acid	$C_{17}H_{31}COOH$	2
Linolenic acid	$C_{17}H_{29}COOH$	3
Clupadonic acid	$C_{17}H_{27}COOH$	4

also with glycerol to produce glycerides, which are of the semi-solid or liquid kind (oils). As a rule it may be said that the more doubly bound pairs of carbon atoms in a molecule of acid, the lower its melting point and that of the glyceride. It is worthy of note that the position occupied by one or more of these ethylenic bonds in the long carbon chain is important from many points of view. In castor oil is found ricinoleic acid, which resembles oleic acid except that it possesses an OH group in place of one of the hydrogen atoms, its formula being therefore $C_{17}H_{32}OH \cdot COOH$.

359 Classifying Fats and Oils

In addition to forming an important division of natural food-stuffs, fats and oils have great industrial application. Those glycerides which contain linoleic or linolenic acids, or both, have the peculiar property of polymerizing when exposed to oxygen. The polymer-oxidation products are more or less hard, resinous-appearing masses which find use as waterproofing agents and paints. Hence fats and oils are classified in the following manner:

(1) *Non-drying*: those which do not thicken or harden on exposure to the atmosphere.

(2) *Semi-drying:* thickening but not hardening as in (3); they may contain linoleic or a similar acid.

(3) *Drying:* thickening and eventually producing hard films on exposure to the atmosphere; linseed oil, a common example of a drying oil, contains considerable linolenic as well as linoleic, oleic and palmitic acids.

Non-drying oils occur in land animals particularly, and in the majority of plants. Examples of them are the well-known beef, mutton and pork fats and the oils obtained from the palm, olive, cottonseed, etc. Their principal use is as food and in food preparations, as well as lubricants. Semi-drying oils are obtained from a few plants and from marine fish. They are used for such purposes as waterproofing and softening leather. Drying oils are few in number. In addition to linseed oil obtained from flax seed, tung or China wood oil has of late years found considerable application as a vehicle for pigments because of the superior finish it imparts to a film of paint. By a suitable admixture with cork and other ingredients, drying oils may be used in the manufacture of flexible floor coverings of great durability.

360 Extracting Fats

There are three general methods in use for extracting fats and oils from their various sources:

(1) *By pressure.* This produces a high grade of oil and is especially applicable to seeds, nuts, etc.

(2) *By heat.* Heating, or rendering as it is usually called, is particularly suited to the tissues of animals and fish, where the fats are solid or semi-solid, as in separating lard from the tissues of the hog.

(3) *By solvents.* Though this method is very efficient, it requires subsequent evaporation and recovery of the solvent used, such as benzene. The product is not desirable for feeding purposes.

361 Clarifying Fats

Most fats are colored and contain sedimentary matter. The sedimentary matter may be separated on standing by decantation and filtration, or by special precipitating agents; the coloring matter, if undesirable, requires the use of one or more bleaching agents.

Many natural fats also contain free acids to some extent. In certain instances they may be desirable; but acidity (or rancidity) is extremely detrimental to metal surfaces, and such oils may not be used as lubricants. Rancidity may be temporarily corrected by

the addition of mild alkalies such as lime, but fats once rancid tend to become so again.

362 Common Fats

Among the commonest fats which form part of the diet of human beings are butter, olive oil and lard. Recently the cultivation of the soybean on this continent has increased the use of soybean oil as an edible fat. The chief sources of olive and palm oils are Italy, Spain and the West African Coast. Cottonseed oil, which very closely resembles olive oil, is extracted from the cottonseed.

363 Plant Synthesis of Fats

It is not known by what steps fats are synthesized in the plant kingdom. Every species of plant or animal appears to possess in its total fat content an arrangement of fatty acids, both in number and kind, which is characteristic of that species. In general marine fish are at one end of the scale and such obviously land animals as man, the dog, the cow, at the other. And, just as the naturally found fatty acids have even numbers of carbon atoms, so the natural oxidation of fats which are eaten as food removes two carbon atoms at a time; thus an acid of C_{18} would by even steps be degraded to a C_4 acid, butyric. A failure in the further oxidation of this acid is a concomitant of diabetes. By whatever means plants may synthesize fats, it is known that animals can perform this task by making use of carbohydrates. By far the most of the fats produced today are used as foodstuffs, the second use from the point of view of quantity being in the manufacture of soap and its valuable by-product, glycerol.

364 Hydrogenating Fats

The discovery by Sabatier of the catalytic value of finely divided nickel in adding hydrogen to doubly bound carbon atoms has resulted, *inter alia*, in the easy hydrogenation of such oils as possess the ethylene linkage (§ 303). Thus some oils, not generally accepted as edible, may be transformed into solid fats practically identical with lard or beef or mutton fats. Such products need cause no alarm to the housewife who may be inclined to regard whatever is so processed as synthetic and therefore untrustworthy. Indeed

their mode of preparation and freedom from rancidity may result in their being far more suitable for cooking purposes than the natural fats, which, when all is said and done, were not originally designed by nature to withstand the temperatures of the frying pan.

365 Hydrolysis of Fats

Natural fats and oils are always mixtures of many glycerides, to determine whose complexity requires much labor and ingenuity. In consequence they do not show the characteristics of pure compounds; for example, they do not melt sharply but soften over a long temperature range. Though it is possible to synthesize many glycerides, by far the most of our knowledge of fats has been obtained by the hydrolysis of naturally occurring fats. This process of hydrolysis is the reverse of that given for the synthesis of tributyrin and is quite common where fats are left in contact with water or even moisture. For example, a sample of pale yellow butter, which has not been artificially colored, turns hard and white if allowed to weather; at the same time it develops the disagreeable taste and odor usually associated with rancidity. What occurs in such an event may be exemplified by the equation:

$$\begin{array}{llllll} CH_2OOC\cdot C_{17}H_{35} & & HOH & & CH_2OH & \\ | & & & & | & \\ CHOOC\cdot C_{17}H_{35} & + & HOH & \rightarrow & CHOH & + 3C_{17}H_{35}COOH \\ | & & & & | & \\ CH_2OOC\cdot C_{17}H_{35} & & HOH & & CH_2OH & \\ \text{Tristearin} & & \text{Water} & & \text{Glycerol} & \text{Stearic acid} \end{array} \tag{136}$$

Thus the fat tristearin is hydrolyzed (by reaction with water) to give free glycerol and stearic acid.

366 Saponification

This process of hydrolysis is slow and is materially hastened by the action of sodium or potassium hydroxide. In this case, however, the sodium or potassium salt of the acid and not the free acid is obtained in addition to the alcohol glycerol. This variation of the process of hydrolysis is known as saponification (§ 283). The treatment of natural fats and oils in this way to produce soap is responsible for the term *saponification*, which actually means soap making.

SOAP

367 Detergents

Common soaps result from the hydrolysis of fats by means of such alkalies as sodium and potassium hydroxide, the former producing hard soaps and the latter soft ones. The process of soap making may be exemplified by treating tristearin with an aqueous solution of sodium hydroxide or soda ash:

$$C_3H_5(C_{17}H_{35}COO)_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3C_{17}H_{35}COONa \quad (137)$$

The products of this reaction are glycerol and sodium stearate. The glycerol remains dissolved in the water used to dissolve the alkali; the soap floats to the top and is coagulated by the addition of common salt. Various fats and oils are used in soap manufacture. The soap thereby prepared is skimmed off, washed and pressed into cakes for commercial use, and the glycerol is extracted from the aqueous residue and used to manufacture nitroglycerin, etc. Floating soap may be made by filling it with air bubbles; colored, scented soaps require merely the addition of the appropriate dyes and perfumes prior to pressing into cakes.

Soaps owe their cleansing (detergent) power to the fact that they concentrate at any water-oil interface, reduce the surface tension, and lead to emulsification of the oil (and any dirt particles embedded in it) in the water. The opalescent appearance of soapy water is due to colloidal particles of soap and of fat acid produced by hydrolysis of the soap. Sodium stearate may be used to exemplify this hydrolysis:

$$C_{17}H_{35}COONa + H_2O \rightarrow NaOH + C_{17}H_{35}COOH \quad (138)$$

Agitation produces bubbles, which are merely pockets of air, covered and separated from each other by thin layers of colloidal solution spread over the large surface of the bubbles. In these layers the dirt is picked up and so can be removed from the material to be cleaned.

Some natural waters tend to produce little or no lather in contact with ordinary soap; such waters are called "hard." *Hardness* is a term used to indicate the kind and degree of dissolved salts in natural waters. It is based on the ability of such water to form a

lather with soap. If a quantity of distilled water in a measuring cylinder is treated with, say, one ml of a saturated soap solution and well shaken, a head of soap lather will be produced whose volume is easily read. This lather will "stand up" for a considerable length of time. A so-called hard water will produce much less lather, if any at all; so that natural waters may be compared with pure water. The reason for the production of less lather by a hard water is seen from the following equation:

$$\underset{}{MgSO_4} + \underset{\text{Soluble soap}}{2\text{Na palmitate}} \rightarrow \underset{\text{Insoluble soap}}{\text{Mg palmitate}\downarrow} + Na_2SO_4 \qquad (139)$$

Here magnesium forms an insoluble, gummy mass with the acid radical of the soap, which is unable to produce the required lather.

This soap test is an empirical one, but its importance lies in the fact that it does detect the presence of those salts which interfere with the cooking of vegetables, the laundering of clothes and the efficient operation of a continuous flow water boiler.

If the hardness of a sample of water can be removed by boiling, this hardness is called *temporary;* if not, it is called *permanent.*

Temporary hardness is caused by the presence of the bicarbonates of magnesium or calcium or both. Lake and river water which contains CO_2 may flow over limestone beds and dissolve the limestone thus:

$$\underset{\text{Insoluble}}{CaCO_3} + H_2O + CO_2 \rightarrow \underset{\substack{\text{Soluble calcium}\\ \text{bicarbonate}}}{Ca(HCO_3)_2} \qquad (140)$$

On being heated, calcium bicarbonate is decomposed thus:

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow \qquad (141)$$

This produces a deposit of calcium carbonate which adheres to the bottom of the boiler or kettle. If sufficient of this scale accumulates it may result in overheating of the metal bottom of the boiler with consequent blow-out at some time.

This temporary hardness may be removed not only by boiling but also by the prior addition of slaked lime (calcium hydroxide):

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O \qquad (142)$$

This removes the calcium salt so that it does not accumulate in a boiler. But an excess of lime can be harmful to a boiler.

Permanent hardness is caused by the sulfates of calcium and

magnesium. The addition of washing soda (Na_2CO_3) removes this type of hardness thus:

$$MgSO_4 + Na_2CO_3 \rightarrow MgCO_3\downarrow + Na_2SO_4 \qquad (143)$$

When the magnesium and calcium are precipitated as carbonates, the sodium sulfate remaining does not make the water hard.

In household washing a large amount of soap will eventually soften the water by precipitation of the magnesium and calcium palmitate; but this is very wasteful of the soap, and the insoluble soaps so formed may not be readily removed from the clothes. Under such circumstances the dried, ironed clothes will eventually become brittle and discolored.

A very efficient household unit for softening water makes use of a solid substance known as *permutit*, a zeolite, having such a formula as $Na_2Al_2Si_2O_8$ (Na_2Z for short), properly packed in a convenient tank attached to the water supply. With dissolved calcium sulfate it reacts as follows:

$$Na_2Z + CaSO_4 \rightarrow CaZ\downarrow + Na_2SO_4 \qquad (144)$$

This calcium zeolite can be changed back to the sodium salt by letting it stand in contact with a concentrated salt solution:

$$CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2 \qquad (145)$$

The excess of salt is then flushed out of the container and it is ready for use again.

PAINT

368 The Composition and Action of Paints

Drying oils are of great importance in the paint and varnish industries. A paint contains mainly four constituents: (1) the oil or vehicle, (2) a finely divided solid with much covering power or body, the best being white lead, (3) a volatile liquid to act as a thinner and (4) a pigment or colored solid to give, on drying, the desired color. Frequently a fifth substance is added to accelerate the drying. A film of such paint spread over a surface dries rapidly at first owing to the evaporation of the thinner, and then more slowly. This slow stage involves a dual process—the oxidation by the oxygen of the atmosphere of such esters in the oily vehicle as contain doubly bound carbon atoms, and the addition of such

oxidized esters one to another to form large, insoluble molecular aggregations, called polymers. This gives a hard but pliable film in which are embedded the white lead base and the pigment. Oils most frequently used are linseed, tung (China wood), oiticica and a dehydrated castor oil.

The manufacture of a paint involves many important factors besides those indicated above. The vehicle, for example, may be required to withstand considerable weathering where obviously water paints would be useless, thus calling for a careful choice or blending of drying oils. Moreover, the final film must not be hard enough to crack or soft enough to run in hot weather.

Oils which dry naturally always contain some palmitin and olein, which do not tend to harden on exposure to air and are of assistance in keeping a dried film pliable.

To give covering power or body to a paint, white lead (lead hydroxy carbonate) has been used for fully twenty centuries—Cleopatra is believed to have used it as a face powder. Its value as body to paint excels that of all other known solids; but this value depends largely on the method of manufacture. Second to white lead is zinc oxide; and a special preparation of zinc sulfide and barium sulfate, called lithopone, has also been used. More recently titanium oxide (TiO_2) has tended to replace these others, since, in addition to good body, it does not suffer such chemical attack as would be detrimental to the others and to white lead in particular.

In order that paints may be spread by either a brush or a spray, some liquid in which the vehicle is soluble is added as a thinner. It may be turpentine, benzene or mixtures of cyclic hydrocarbons such as naphtha; this thinner should be quite volatile so as not to retard the drying unnecessarily.

The pigment will of course vary with the color required. The chromates of lead and barium, for example, are yellow, one iron oxide is reddish yellow (litharge, PbO) whereas a ferrocyanide of iron is blue, Prussian blue, $Fe_4\,[Fe(CN)_6]_3$, and so on. Coloring matter is frequently used in the form of lakes (§ 379).

To increase the rapidity at which drying takes place the salts of manganese, cobalt, etc., and certain organic acids are added in small quantities. Their function is chiefly catalytic, since they probably act as carriers of atmospheric oxygen, which plays such an important part in the complex drying process. In black paints

finely ground graphite replaces white lead or its equivalent, and since graphite is not readily attacked by ordinary reagents the color is obviously permanent.

369 Varnish

The essential difference between a paint and a varnish is that the varnish contains some resin, whether natural or synthetic, in place of white lead. Varnishes may, therefore, be transparent and translucent, serving to protect what is underneath without imparting any color to it. The resins, of which ordinary rosin is an example, are hard, relatively insoluble masses of organic material of vegetable origin. Upon their successful solution in, and blending with, a drying oil and a thinner depends the final finish. Within recent years a large number of so-called synthetic resins, or rather compounds of high molecular weight and of physical properties similar to those of natural resins, has appeared on the market. They are gradually replacing the others, chiefly because of their greater adaptability and variety.

Cellulose acetate lacquers are not in the same chemical category as paints and varnishes, since the films they give (exclusive of any pigment) are caused solely by the evaporation of the solvent (thinner), leaving the dissolved cellulose acetate behind. The presence of a small amount of some non-drying oil prevents cracking of the dried film; this is called a *plasticizer*.

370 Summary

Fats and oils, in the strictly chemical sense of the terms, are esters of glycerol and fat acids. They are products of both animal and plant life. The terms are interchangeable, a fat being a semi-solid whereas oils are usually more or less fluid at ordinary temperatures.

The constitution of a fat is determined by hydrolysis and saponification since the alcohol is the same in all fats; fats are frequently called glycerides. This name helps to differentiate such oils from the liquid mixtures of hydrocarbons obtained from petroleum and erroneously called oils.

The constituent fat acids determine the properties of the fat. The harder fats contain a larger proportion of saturated fat acids, whereas unsaturated acids give more fluid fats.

The presence or absence of unsaturated fats also permits a classification into drying, semi-drying and non-drying. Drying is the hardening of a fat on exposure to oxygen or the atmosphere. Fats containing linolenic acid (with three ethylene bonds) harden rapidly in air, linseed oil being a good example of such a fat. Fats containing little unsaturated acid do not dry (for example, oleic acid) and may be used as food. Fats displaying an inter-

mediate amount of unsaturation, as certain fish oils, are semi-drying, and their chief use is in waterproofing leather, etc.

Fats and oils may be extracted from their sources by pressure, by heat or by solvents. Most fats need decolorizing and clarifying before being ready for use.

Fats with much unsaturation are liquids; and when they are saturated by means of hydrogen (hydrogenation), the product is more or less identical with the harder natural fats.

The saponification of fats gives glycerol and soaps. Soaps are used for cleansing; glycerol is converted to nitroglycerin, the explosive.

Washing water may be "hard" or "soft," depending on its behavior with soap. Hardness may be temporary or permanent, depending on what salts are dissolved therein.

Questions

1. Write graphical formulae for tributyrin, triolein and tristearin.
2. What is involved in the saponification of a fat? Illustrate.
3. What is meant by the term *drying* as applied to an oil?
4. What is a paint? What kinds of constituents does a paint contain, and what is the purpose of each?
5. How does soap aid in cleansing?
6. What do you understand by the "hardness of water"?
7. How may this hardness be removed if (*a*) it is temporary and (*b*) it is permanent?

26

Explosives—Dyes—Pharmaceuticals

EXPLOSIVES

371 Defining an Explosive

An explosive is a substance, or mixture of substances, which is capable of changing, under the proper stimulus, from a small volume to an extremely large one in a short space of time. Upon the magnitude of this volume change and the length of time involved depends the value of an explosive. Explosives are highly endothermal bodies which require little stimulus in order to decompose into more stable substances with the release of energy.

Charges of explosive, whether used as propellants as in guns or for blasting purposes, are set off by a detonator. It is a small quantity of a compound, such as mercury fulminate [$Hg(ONC)_2$], which is packed in a small metal cylinder open at one end. A slight mechanical shock or flash suffices to explode the detonator, which in turn transmits a shock to the explosive charge, bringing about the main explosion.

To be good an explosive must be chemically stable under ordinary conditions, easily manufactured and safe for transportation. In addition it must give the desired results. As a propellant it must propel without undue shattering; as a shattering agent it must conform to the use demanded, whether in the lifting of stumps or in the destruction of a war vessel or a mass of rock. Some explosive materials are mixtures of ingredients such as the above, whose different characteristics give the best results for the work to be performed.

Thousands of tons of high explosives are used annually for such domestic purposes as clearing land, mining and digging canals,

apart from the amounts set aside, or actually employed, for war purposes. Some raw materials required are glycerol, cellulose, benzene and toluene and nitric and sulfuric acids. They involve, respectively, available supplies of fats, cotton, bituminous coal, nitrates or nitrogen fixation plants and sulfur, either free or combined as in pyrites. Any nation that aims at industrial self-sufficiency has need of these essentials.

372 Gunpowder

This is an intimate mixture of finely divided carbon, sulfur and potassium nitrate—all solids. On ignition by a spark the potassium nitrate is decomposed, handing on its oxygen to the carbon and sulfur to produce large volumes of the oxides of carbon, sulfur and nitrogen. These gases occupy a large volume, which is further increased by the heat produced in their formation, providing a means of propelling a projectile. But the time involved in this volume change from solid to hot gases is long compared with certain other explosives, so that the shattering effect is not great.

373 Nitroglycerin

It may be made by reacting glycerol with nitric acid in the presence of sulfuric acid according to the following equation:

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 \rightarrow \begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array} + 3H_2O \tag{146}$$

It is thus the trinitrate of glycerol.

It is an oily liquid which, when detonated, decomposes with great velocity to give extremely large volumes of gases, the oxides of carbon, hydrogen and nitrogen. Its manufacture is carried on with the utmost precaution. When prepared for use, it is absorbed in an inert solid, such as powdered china clay and sawdust. In this way various strengths of explosive material can be prepared, reducing the danger of handling and tending to slow down the rate of explosion. Such preparations, known as *dynamite*, are used most extensively in mining. Because of its great shattering effect it is not used alone as a propellant for projectiles.

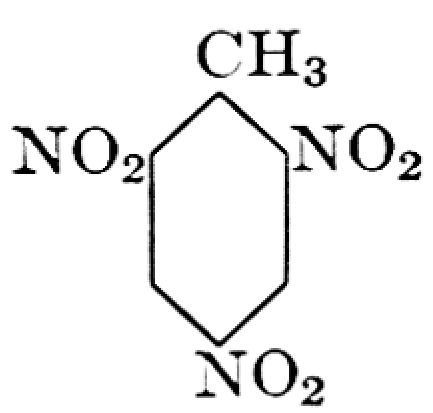
374 Guncotton

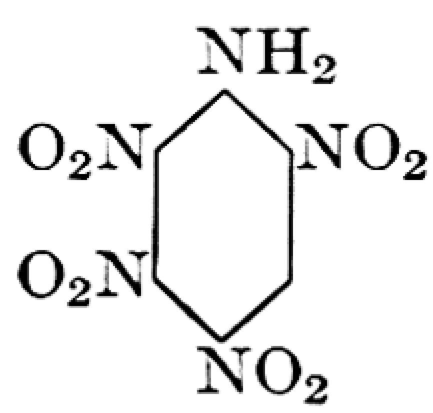
If pure cotton fiber is treated with nitric and sulfuric acids, various cellulose nitrates may be obtained according to the number of nitrate radicals attaching to the $C_6H_{10}O_5$ unit of the cellulose. Guncotton has the formula $[C_6H_7O_2(NO_3)_3]_n$, and the finished product closely resembles cotton in appearance, but burns more rapidly. When suitably packed in a small space, guncotton may be detonated with explosive violence, and under various names is widely used as a propellant for large shells. It is a high explosive, but its rate of decomposition does not involve the shattering so characteristic of dynamite. This is the commonest of propellants and forms a very satisfactory filling for shells when mixed with the easily decomposed ammonium nitrate.

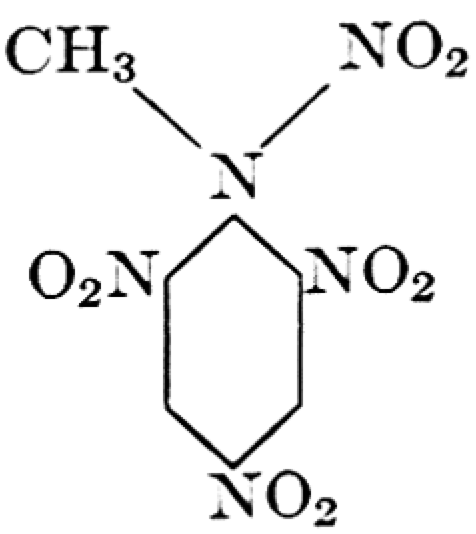
Cellulose nitrates having a small content of nitrate are called *pyroxylin,* a solution of which in camphor is known as celluloid, and a solution in alcohol and ether as collodion.

375 Other Explosives

Below are shown the formulae of three wartime explosives prepared from benzene or toluene and nitric acid.


T.N.T.


T.N.A.


Tetryl

T.N.T. is the abbreviation of trinitrotoluene, the common constituent of explosive shells. T.N.A. is tetranitroaniline and tetryl is trinitromethyl-nitroaniline or tetranitromethylaniline. Their structure is noteworthy in that each possesses a nitro radical in the 2,4,6 positions of the benzene ring. The same statement is true of picric acid, used before the introduction of T.N.T. Picric acid has a formula like that of T.N.T., except that it has an —OH in place of the —CH_3. It is a weak acid, fairly soluble in water, may be used as a dye and has considerable antiseptic value.

A more recent explosive, R.D.X., has a greater shattering effect than any of the above.

DYES

376 Dye History

Prior to the latter part of the nineteenth century dyes were obtained by extraction from both plant and animal matter, though chiefly from plants. This was true in all the civilizations of which we possess a record, and it is still the method of obtaining dyes among primitive tribes, for example, the Eskimos and North American Indians. Principal among these natural dyes were indigo and cochineal. However, in 1856 Perkin (the Elder) in England synthesized mauve, and in 1884 von Baeyer in Germany synthesized indigo. By the end of the nineteenth century the trade in vegetable dyes had largely given place to the synthetic dye industry, which, up to 1918, Germany built to first place in the world. These changes have come about through the utilization of benzene and toluene, both by-products of the destructive distillation of coal.

377 What Is a Dye?

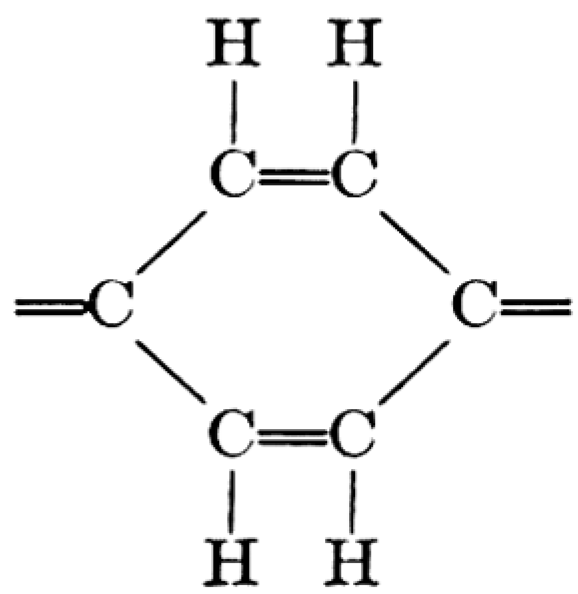
Any colored substance is not necessarily a dye. A dye may be defined rather as a substance which imparts a particular color to some object not so colored. Thus a colorless dyestuff may unite with a fabric to give a highly colored product, that is, the object to be dyed enters largely into the scheme of things. So dyeing may be classified as two separate types: (1) where the dyestuff actually forms a new chemical compound with the material to be dyed; and (2) where the dye is merely absorbed or set mechanically within the fibers of the fabric to be colored. Thus cotton, the neutral carbohydrate, differs from silk and wool, which are nitrogenous substances amphoteric in nature, that is, capable of acting either as an acid or a base. In silk and wool a dye which is a base would form a compound with the acid, or an acidic dye would form a compound with the base, in each case producing a new colored chemical compound. Some dyes combine with cotton directly to form a colored compound. In other instances the cotton must be impregnated with a *mordant*, such as aluminum acetate; on being treated with the dye the material becomes colored owing to the reaction between the dye and the mordant, the resulting pigment being retained mechanically within the cotton fibers. Again, the material may be impregnated with a dyestuff giving an uncolored product, which on subsequent oxidation gives the desired color.

Or again the material may be treated with one of two ingredients, which together will ultimately give the dye; it is then transferred to another bath and treated with the second ingredient, whereupon it becomes the correct shade.

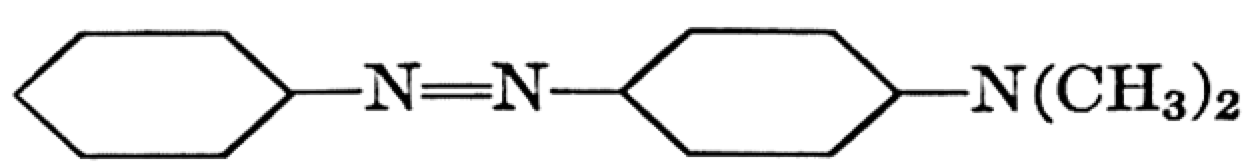
378 A Theory of Color

A simple theory of color put forward by De Witt will serve to picture the structural requirements of dyestuffs in which the following combinations frequently appear:

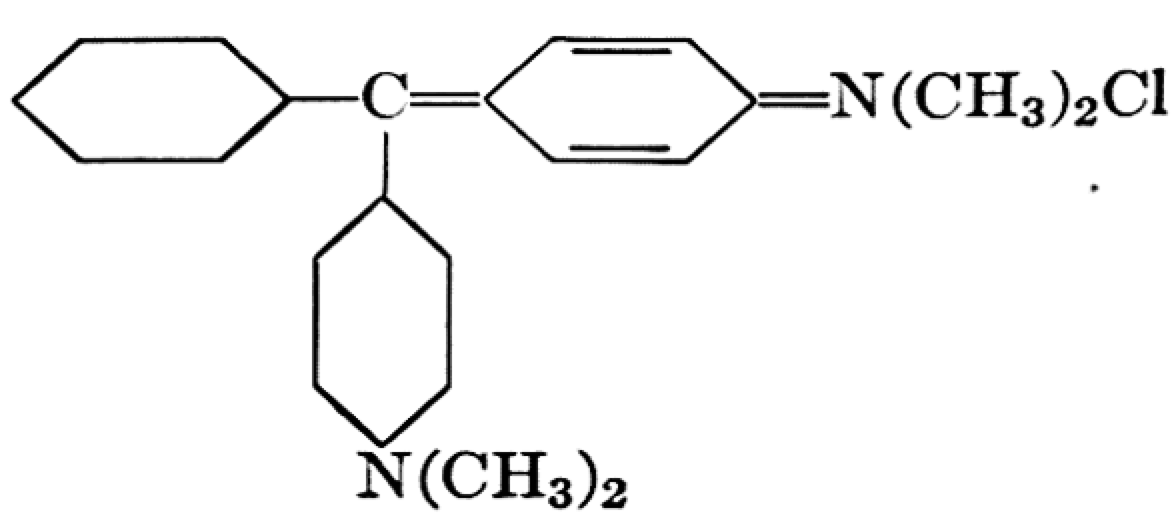
—N=N—



These are called azo and quinoid, respectively. They occur in many dyes, and on them depends the ability of such dyes to produce color; hence they are termed *chromophores*. But in order that color may arise from the chromophore foundation, other groups, such as —OH and —NH_2, are essential, the latter being called *auxochromes*. Dyes have complex structures and long names, which are frequently shortened for trade purposes. Below are some simple examples of dyes given to illustrate this theory:



This is butter yellow, a food coloring; it is an azo compound.



This is malachite green, a quinoid dye; the auxochromes are —$N(CH_3)_2$ and =$N(CH_3)Cl$.

379 Lakes

If a dye is added to, say, aluminum hydroxide (itself a mordant), a colored, insoluble precipitate is produced. These precipitates are called lakes, and are much used as pigments in the manufacture of colored paints.

PHARMACEUTICALS

380 Bacterial History

Pharmacy and medicine have marched side by side since the earliest times, the doctor and the druggist being one and the same person on many occasions. But their development, as we now know these art-sciences, awaited the discovery of the microscope. It is probable that Roger Bacon [1] in the thirteenth century had attained that goal. Four centuries later van Leeuwenhoek reported having observed living organisms in saliva in the course of experiments with a microscope of his own making. But it was not until the last century that Pasteur discovered the bacterial origin of disease. Prior to this, the theories to account for disease were concerned either with the ancient idea of demoniacal possession or with the presence of humors in the blood resulting from a deficiency or surplus of certain real and often visionary ingredients.

Following Pasteur's lead, Lister made the first real advance towards antiseptic surgery, tending towards eliminating pathogenic (disease-producing) bacteria from exposed tissues during operations. Early surgical methods had previously included cauterization by hot irons to stop bleeding, but this, though detrimental to bacterial life, was hardly commendable in every instance. Lister relied on washing both surgical instruments and the skin to be treated with phenol (carbolic acid) to destroy the microorganisms which might be harmful to the patient. This washing was not entirely effective, but it decreased the post-operational mortality rate and paved the way for further improvements in this direction.

381 Antiseptics and Disinfectants

For purposes of sterilization of instruments, etc., heat treatment above 100°C is eminently satisfactory; but this is obviously un-

[1] J. N. Leonard, *Crusaders of Chemistry*, p. 47, Doubleday, Doran, 1930.

suited to living tissues. Modern methods rely on powerful but non-corrosive solutions to remove bacteria, and sterile dressings to keep them away. Since the action of pathogenic bacteria is dependent upon their reproduction, any reagent that will prevent this reproduction without a corrosive action upon living tissues will satisfy the requirements of an *antiseptic.* Should such a reagent destroy the bacteria at the same time, so much the better. A distinction is therefore drawn between an antiseptic and a *disinfectant,* in that the former may be regarded as preventing bacterial growth whereas the latter destroys bacteria outright. The requirements of a good antiseptic are that it be effective and non-corrosive. One of the earliest used was phenol; but it does not fulfill either of these requirements, being, except in very dilute solution, highly corrosive to human tissue.

382 Some Common Disinfectants

Some common disinfectants now in use are chlorine, sulfur dioxide, formalin, phenol, the cresols, hypochlorites and chloride of lime. The first of these is commonly added in very small quantities to the water system of large cities. Here hypochlorous acid is formed, and the subsequent evolution of oxygen kills the bacteria present; and the very small quantity of hydrochloric acid remaining in the water has no deleterious effect when taken internally. Sulfur dioxide was formerly used for fumigation but has been replaced by formaldehyde dissolved in water-alcohol (formalin). Phenol is now seldom used, though aqueous solutions of the cresols [2] under a variety of trade names can be used externally on the human body with more germicidal effect and less danger of corrosion. Aqueous solutions of sodium or potassium hypochlorite are excellent disinfectants and are widely employed as such in laundries, wherever their bleaching action is not detrimental to the colors and fabrics being washed. Chloride of lime prevents decay of refuse and deodorizes such refuse, because of its ready evolution of chlorine even when dry.

383 Common Antiseptics

Antiseptics are of many kinds. Ethyl alcohol in water is a very efficient one. Iodine, dissolved in alcohol, potassium iodide and

[2] Cresols are hydroxy derivatives of toluene.

alcohol, known as tincture of iodine, is often used, although it is somewhat corrosive if concentrated. Iodoform, silver nitrate, organic silver compounds, silver iodide and boric (boracic) acid are employed for various antiseptic purposes, though usually externally and in dilute solution.

Although phenol is corrosive, related compounds are more powerful in their antiseptic value and much less corrosive, so that they may be used internally as well as externally. Chloramine T. is representative of a type which resembles sodium hypochlorite. Certain dyes, like malachite green, are in present use as antiseptics. The characteristics of a good general antiseptic are that it can be used internally, will give prolonged action and is noncorrosive. Modern research has produced a large number of such compounds to replace the former ones of lesser value, but for external purposes none is more effective than a 5 per cent iodine solution.

384 Pharmaceuticals

Medicine is the art-science which deals with the prevention, cure or alleviation of disease. In its long history it has had many kinds of practitioners. Of late years, however, a close relationship has grown up between the doctor and the pharmacist, that is, the one who is concerned with the preparation, preservation and dispensing of such remedies as the doctor prescribes. Consequently, the word *pharmaceuticals* has come into use, a word designed to cover the vast range of materials so prescribed. Back of the pharmacist today is a large number of organizations preparing these materials, so that the modern pharmacist is not obliged to follow his predecessors and go out into the fields to collect the raw materials from which to make his elixirs and decoctions. The history of over twenty centuries lies behind the modern pharmacist. In that time many words have found their way into our vocabulary, and not without some confusion at the present time.

Pharmacology is described as the science of *drugs*, which in turn is defined as substances used medicinally. At the same time the word *therapeutics* means that part of medical science pertaining to the discovery and application of remedies for disease. Since all the materials included under these heads are designed to restore

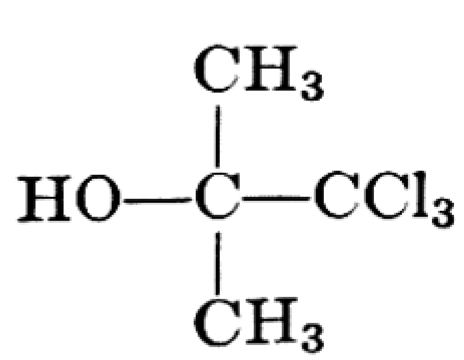
the normal functioning of human organs, it is now common practice to speak of a substance used in medicine as having a physiological effect. Although no general rule is so far apparent, there are many instances in which physiological effect seems to be aligned with chemical structure. Examples which follow here will indicate this relationship.

These definitions may help the beginner. A *soporific* is an agent to induce sleep (so is a *hypnotic*). An *analgesic* produces insensibility to pain. An *anesthetic* produces insensibility by partial or complete loss of feeling, that is, local or general anesthetics. A *narcotic* is a drug which in moderate doses relieves pain and induces sound sleep, but in large doses induces stupor, coma or convulsions.

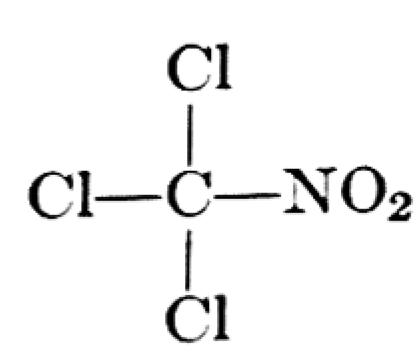
Toxic is an adjective meaning "caused by or pertaining to a poison"; and a *poison* is any agent which, introduced into the animal organism, may produce a morbid, noxious or deadly effect. A *febrific* causes fever and an *antifebrile* or *febrifuge* abates or removes fever. A *diuretic* is designed to increase the secretion and discharge of urine. An *emetic* induces vomiting. A *cathartic* cleanses the bowels (although catharsis means the cleansing of any part of the body). Bacteria are described as germs or microorganisms so that a *bactericide* and a *germicide* are the same thing as a *disinfectant*, that is, a germ destroyer. But a bacterium is not necessarily pathogenic (disease-producing), since many bacteria are vitally necessary, as in the fermentation of alcohol to vinegar and the purification of polluted streams. It is obvious from these generally accepted definitions that it is extremely difficult to draw a sharp line between a pair of these terms.

385 Constitution of Some Important Organic Compounds

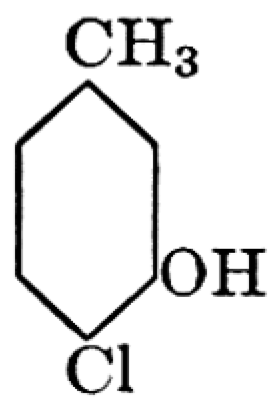
The following structural formulae are a few examples from many which could be given and which may be found in any more advanced textbook. (See, for example, Richter's *Textbook of Organic Chemistry*, Second Edition, Wiley.)



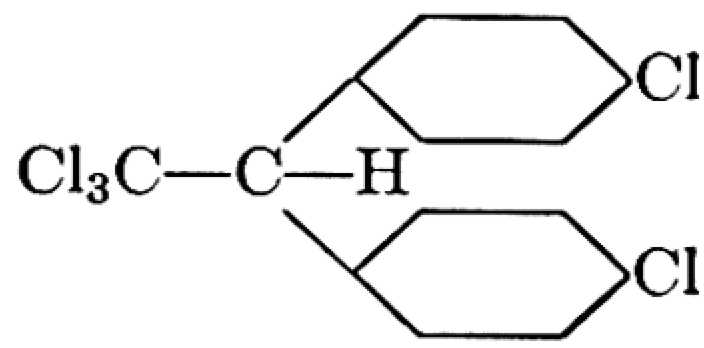
Chloretone, a hypnotic



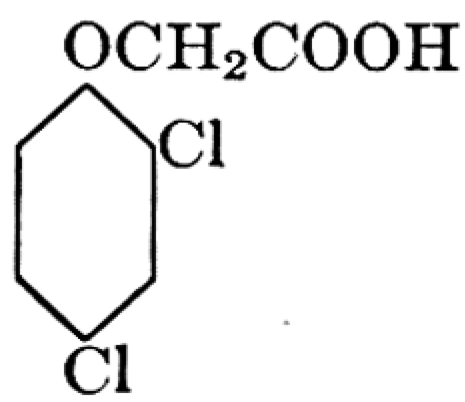
Chlorpicrin, a lachrymator



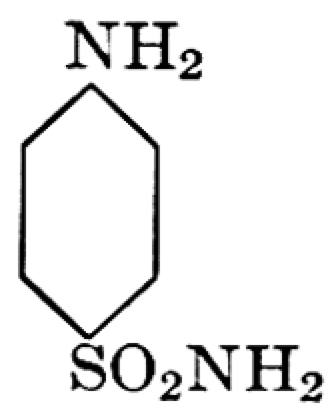
Moldex, textile preservative



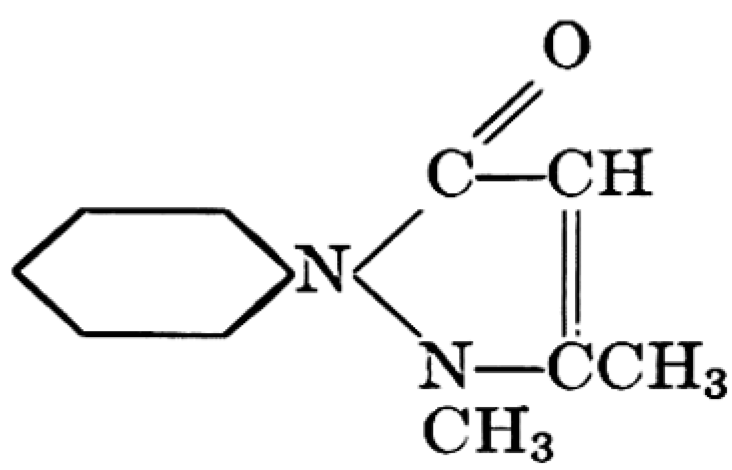
D.D.T., insecticide



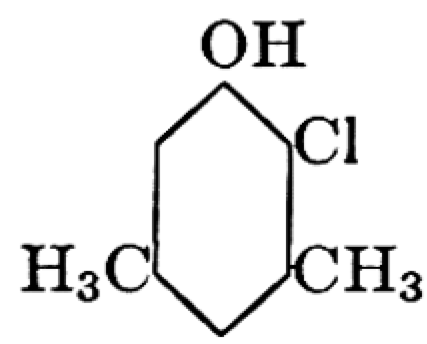
2,4-D., weed killer



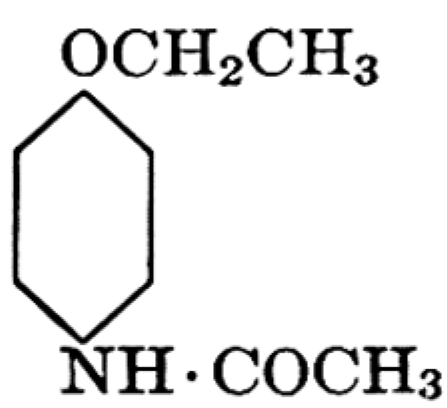
Sulfanilamide



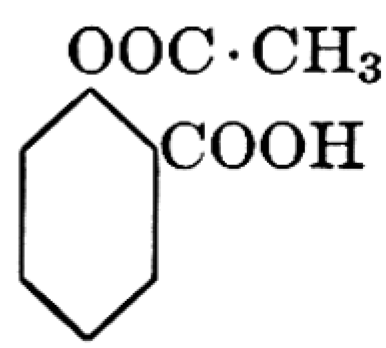
Antipyrene, analgesic



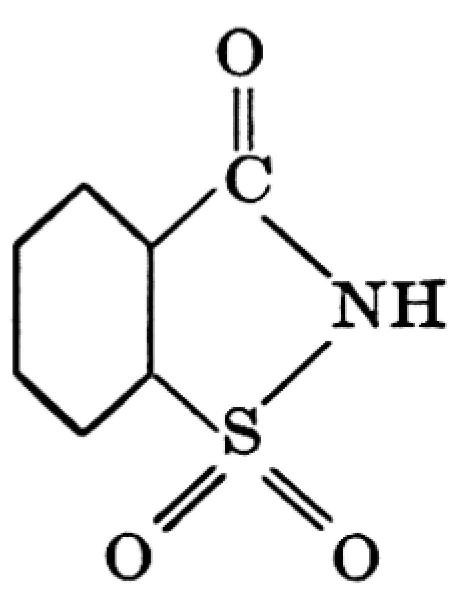
Para-chloro-metaxylenol, antiseptic



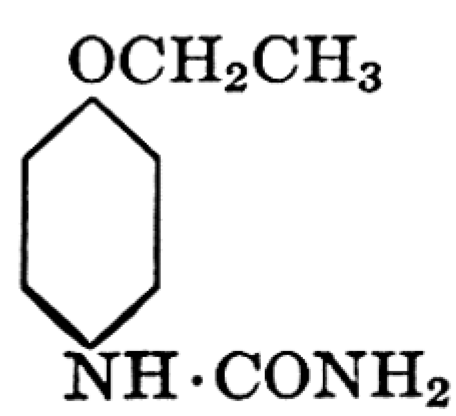
Phenacetin, antipyretic



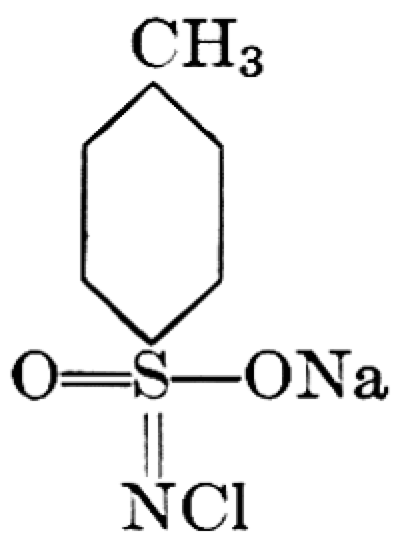
Aspirin, antipyretic, analgesic, antirheumatic



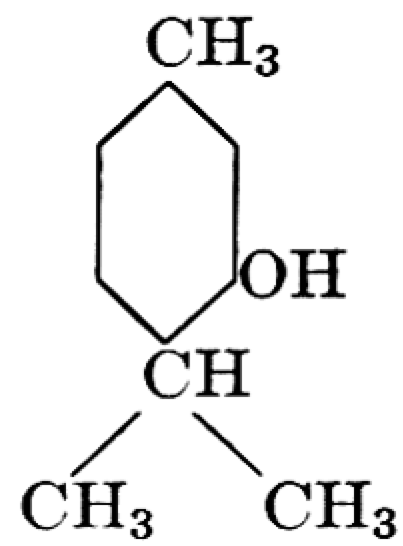
Saccharin, sweetening agent



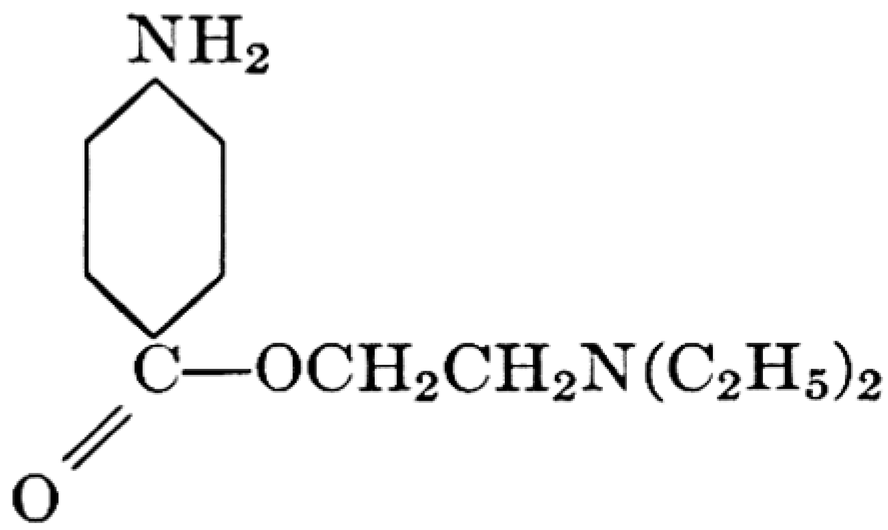
Dulcin, sweetening agent



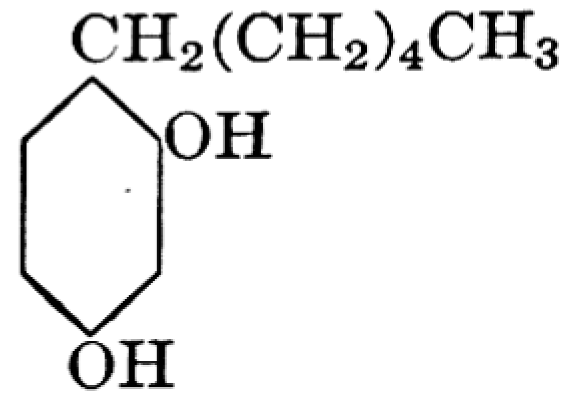
Chloramine T, external disinfectant



Thymol, inhalant



Novocaine, local anesthetic



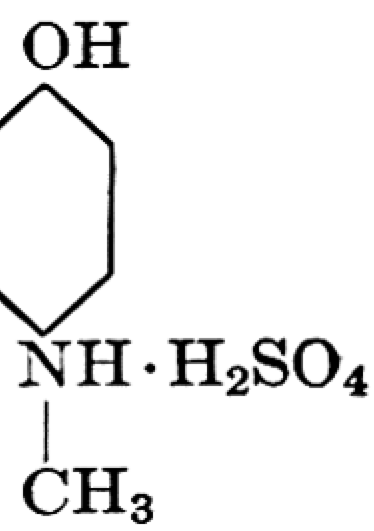
Hexylresorcinol, internal antiseptic

$$CCl_3CH_2OCONH_2$$

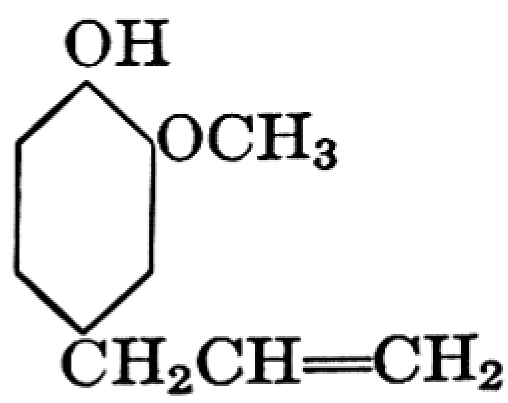
Voluntal, hypnotic

$$\begin{array}{l} CH_3(CH_2)_4\overset{}{C}HCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad NH_2 \end{array}$$

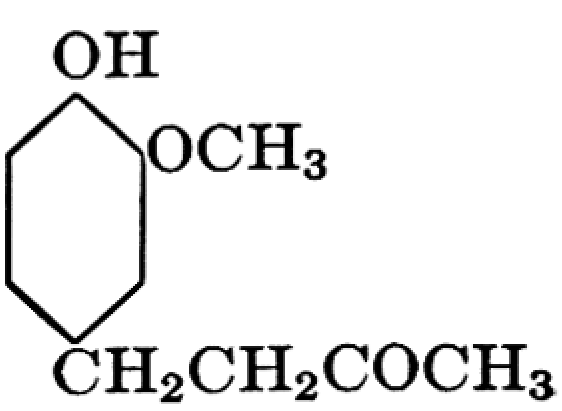
2-Amino heptane, inhalant



Metol, photographic developer



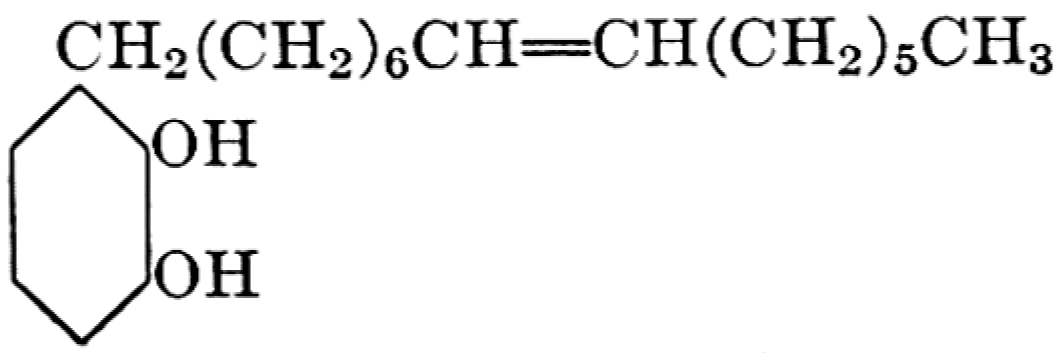
Eugenol, flavoring constituent of cloves and cinnamon



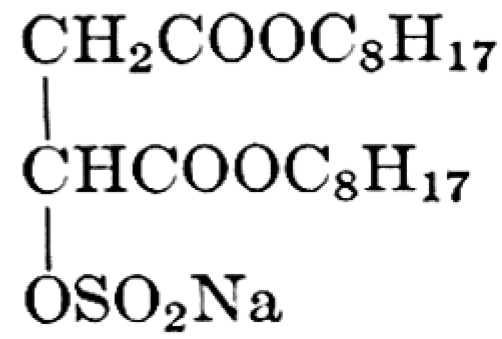
Zingerone, flavoring constituent of ginger root

$$\begin{array}{l} CH_3CH_2CH_2CHOH \cdot CH \cdot CH_2OH \\ \qquad\qquad\qquad\qquad\quad \cdot \\ \qquad\qquad\qquad\qquad\quad CH_2CH_3 \end{array}$$

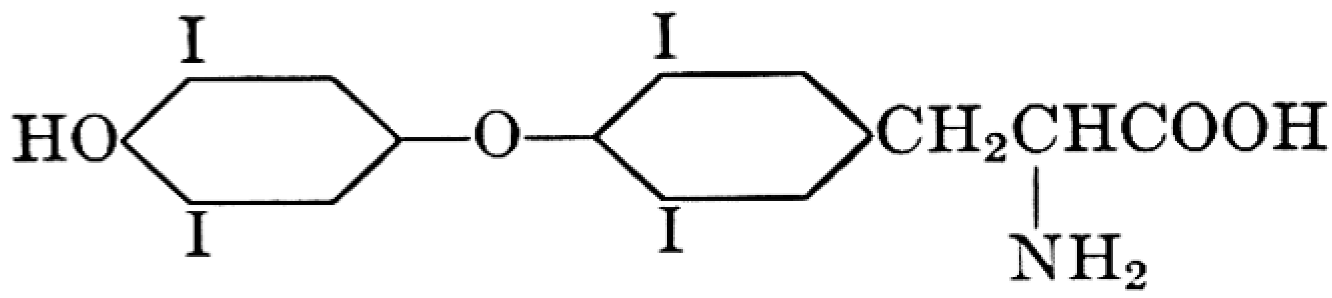
2-Methyl, 1.3-hexanediol, fly-repellant



Urushiol, active principle of poison ivy



Aerosol—O.T., detergent



Thyroxin, essential to health of thyroid gland

386 Summary

An explosive is a substance, or mixture of substances, which may evolve an extremely large volume of hot gases in a short interval of time. Gunpowder, nitroglycerin, guncotton, T.N.T., picric acid, T.N.A. and tetryl are common explosives with varied properties and uses.

A high explosive differs from, say, gunpowder in the shorter interval of time that elapses between detonation and the decomposition.

Most explosives depend upon the instability of nitric acid and its derivatives for their effectiveness.

Dyes are carbon compounds designed to form colored bodies with such materials as cotton, silk and wool.

When the dye gives color by uniting with the material to be dyed, a colored compound is obtained. But if the dye will not form such a compound, it may form one with a mordant with which the fibers of the material are impregnated.

Compounds of dyes and mordants constitute the insoluble bodies called lakes which are used as pigments in paints.

Color depends upon chemical constitution. Certain structures, for example, azo and quinoid, have the power to donate color when reinforced by the presence of simple radicals in the molecule of dye.

Modern pharmaceutical products include a great variety of extracts from the plant and animal kingdoms as well as an increasing number of synthetic substances. These materials cover a very wide range of usefulness, and their structures show a physiological relationship by means of such radicals as amino, amido, sulfonic and chloro, and such compounds as phenol and pyridine.

Questions

1. Define and illustrate the terms explosive, antiseptic, disinfectant and dye.
2. Compare the characteristics of gunpowder and nitroglycerin.
3. What radicals and positions are of significance in an explosive made from benzene?

4. Outline a simple theory of color.
5. What are the azo and quinoid structures? Illustrate.
6. What difference do you see between (*a*) a soporific and an anesthetic? (*b*) an anesthetic and a narcotic? (*c*) the two main types of bacteria?
7. From the list of compounds shown in paragraph 385, draw your own conclusions from chemical constitution and physiological effect.

Part 3

FOOD CHEMISTRY

27

Foods and Their Values

387 Foods in History

The adequate provision of food for himself and his dependents has always been one of man's chief occupations and has been responsible for many large-scale movements of populations from the beginning of recorded time. In tropical and semi-tropical climates, fruits of various kinds have by their profusion made the maintenance of life a much easier task than in more northerly regions. The daily fare of natives of tropical islands continues to be the produce of the sea and of plants, just as it was for their ancestors, who took the fruits of both with little regard for the cultivation of either since nature had been very generous in her provision of each. But in the more northerly parts of Europe, Asia and North America in early times man subsisted mainly by hunting and fishing. When hunting failed he moved on with his family to follow the game or to find new means of subsistence.

The ability to till the soil produced a settled mode of life; and so new communities arose in isolated places, growing in time into nations, whose resulting civilizations left the evidence of their progress in architectural remains when they ceased for one reason or another to exist. Chief among the cultivated plants in Asia Minor and Egypt were wheat and barley, two of the many varieties of grasses, which, selectively cultivated, ultimately formed the basic diet of these early peoples. This cultivation reached a condition bordering on perfection among the dwellers of the Euphrates and Tigris valleys before nomadic invasion and traveling dust storms obliterated these regions from the sequential story of mankind. The records of the Babylonians and the Egyptians have provided us with an insight into the agricultural methods of these peoples; and the story of the early life of the Hebrews under the

Pharaohs shows that they regarded overproduction of barley in the fertile Nile plain as tending to relieve underproduction in less favorable years by a system of carry-over.

388 Animal and Vegetable Foods

Purely nomadic tribes have always relied upon animal foods, as evidenced by the buffalo hunting on this continent, and in Africa and Arabia by the versatile camel, whose milk has been for many centuries a basic foodstuff. In addition, of course, the skin and the flesh (and even the dried dung for fuel) have not been overlooked. Where large stretches of fertile grasslands existed, some nomadic tribes bred sheep and goats and tended them in their grazing, just as one sees it done in eastern Europe today.

Nevertheless, directly or indirectly, man has been dependent ultimately upon the product of vegetation for his subsistence; and it appears to be a fact that the more civilized he has become the more directly he has been dependent upon such grains as wheat, barley, rice and rye. Undoubtedly this dependence was forced upon him, since the acreage necessary to the grazing of cattle for food is much larger than that required for the growth of grains for human consumption; therefore dwellers in large, settled communities became more and more eaters of grain. In more northerly climates, however, where cultivation of the soil is difficult, fish of various kinds forms the basic diet. The Eskimos, whose chances of cultivating the soil advantageously are hampered by too short a summer, are an example. To a great extent, then, the agricultural produce is dependent upon climatic conditions. It frequently happens, however, that in suitable climates the soil is unsuited to agriculture or has been rendered so by too intensive cultivation without regard to replenishment. It is common knowledge that mixed farming, for example, accompanied by the raising of livestock, has for long periods of time prevented the impoverishment of the soil. However, where large tracts of virgin land have raised crops for only a few years without animals to aid in fertilization, such lands have tended to grow sterile and degenerate into desert. Incidentally this very situation, aggravated by drought, is one that is being faced at the moment on the American continent.

389 Food and Transportation

Since the introduction of steam as motive power for transportation the dietary habits of many peoples have changed, especially within the last few years. What formerly was a luxury, enjoyable only on special occasions, has become a necessity all the year round. Transportation by air has materially increased this change. If to these factors are added the modern and efficient canning and freezing methods of industry, we see to what degree present-day diets have become diversified. This is all to the good where health and standards of life are involved.

Thus to the modern table, at a reasonably low price, come the produce of north, east, south and west. Cereals, meats, fish, vegetables and fruits contribute their quota of naturally formed ingredients to the well-being of the natural animal, man.

Whereas our ancestors were content to eat what they could get, accepting what we now know to be deficiency diseases as a punishment from heaven, we now peer into the very core of our foodstuffs to see of what they are made and to try to discover which of them lack what we know our systems require. Hence the world has become food-conscious, and, curiously enough, most conspicuously so on the American continent, where the standard of living has been the highest in the world for many years.

390 The Human Machine

The following pages are designed to present the importance of foods as chemical raw materials to be utilized by a factory (the human body), whose operations are of necessity concerned with maintenance and energy. First, however, a brief description of body parts is essential.

The skeleton is a bony structure, composed largely of calcium phosphate [$Ca_3(PO_4)_2$]; here the various parts are so connected as to permit of movements necessary to the operation of the body as a whole or in part. Parts of this skeleton, like the skull and ribs, are for the protective covering of vital organs. In chemical content, the teeth also belong to the skeleton.

The muscles are fibrous bundles of protein attached to the bones in such a way as to cause them to move when the muscles contract under the influence of the necessary stimulus. Chemically, the muscles show structures similar to that of the nervous system and all the other protein-containing organs with their special functions.

The nervous system, which has its center in the brain, very closely resembles a bundle of telephone wires for the transmission of messages within the system. The muscles, the specialized organs and the nervous system, all largely composed of proteins, contain carbon, hydrogen, oxygen and nitrogen, together with relatively small amounts of sulfur and phosphorus. They represent the three main types of structure which constitute the mass of the human body.

In addition, there are subsidiary parts of varying texture and with special functions. The heart, for example, is a muscular body concerned with pumping the blood throughout the system by means of arteries, capillaries and veins. The eyes, nose, tongue and ears are the organs responsible for sight, smell, taste and hearing; the alimentary canal, in its many parts of mouth, stomach, intestines, pancreas, liver and bile, is concerned with the utilization of food. Furthermore, the lungs act as an exchange for oxygen and carbon dioxide; the kidneys and intestines are concerned with the elimination of refuse. Assisting these specialized organs is a collection of glands with diverse functions.

Assisting the blood stream is the lymphatic system, which has a considerable number and variety of functions. Fat also is found in small or large proportion, depending on several factors. This fat may serve as protection to special organs within the skeleton, or may help to maintain the constancy of body temperature by its insulating capacity.

391 Maintenance and Repair

This entire apparatus, the body, if life is to be maintained and worn out parts replaced, requires a variety of raw materials from sources external to itself. These raw materials are of two general kinds, namely, oxygen, which is admitted by way of the lungs, and food, which is taken in by the mouth. This food must serve not merely to repair the larger working parts of the human machine but also to insure the continuation of operation of each essential part of the food-digesting mechanism itself and, in addition, to supply the machine with energy. By far the larger part of the food intake produces the necessary energy to cause all correlated parts to function, not to mention the performance of external work. It appears, furthermore, that the coordination of all these parts is such that a defect in one part is extremely likely to work towards a breakdown of the entire machine.

This outline presents the maintenance of life as a much simpler operation than it really is. Though the body provides its own furnace, the furnace has to be carefully thermostated under widely varying external conditions, and the whole mechanism has to be automatic to take care of the many sudden demands for energy made upon it. Actually, it is a beautifully working mechanism, not requiring, fortunately, the conscious effort that might be expected of the human race, which has the power of thought and will to go counter to its best interests if it so desires.

392 Foods as Chemicals

The most that the chemist essays to do is to trace the chemical changes that occur in this apparatus and study the factors important to these changes. In this work he has his raw materials, the foods, and as his subject food chemistry, an important branch of the larger subject of vital or biological chemistry.

These raw materials, in addition to water, of which a great quantity is required, may be classified as follows:

1. Carbohydrates	The bulk foods which serve as energy and tissue producers.
2. Fats	
3. Proteins	
4. Inorganic salts	In small quantities.
5. Vitamins	Necessary in minute quantities.

The first three of these raw materials constitute by far the major portion of human foodstuffs; and since their primary function is to provide body energy by means of oxidation, they may be called the *fuels* of the diet. As fuels, then, the maximum amounts of heat which they can produce may be determined in exactly the same way we should find the heat value of a sample of coal or other fuel, that is, by burning in an atmosphere of oxygen. The analogy is a good one since coal contains mainly carbon and hydrogen as combustible elements generating heat, and these three types of food contain the same elements; but they also contain oxygen and nitrogen, which do not contribute any heating effect. Also the end products of the oxidation of carbon and hydrogen are the same in both instances—carbon dioxide and water.

393 Foods as Fuels

This combustion of foods may be carried on in a large, heat-measuring apparatus known as a *calorimeter*, specially designed to permit the burning of the appropriately dried foodstuff in an at-

mosphere of oxygen with all the necessary precautions for correct observation of the heat given out. An exact value can thereby be obtained of the amount of heat any food will give when it is burned to its final products.

When 1 gram of carbon is burned to form carbon dioxide, 8080 calories are given off; similarly 1 gram of hydrogen, burned to produce water, yields 3450 calories. (Where large numbers of calories are used a larger unit is convenient. This is the kilocalorie, written Calorie. 1 Calorie equals 1000 calories.) When these elements are present in a compound and that compound is burned to produce carbon dioxide and water, the same amount of heat is produced as if they were burned separately. If oxygen is present in the molecule (as in these three foodstuffs), it contributes nothing to the heat produced, though its presence requires less added oxygen and materially increases the weight of material to be oxidized. Thus C_6H_{12} will give off just as much heat in its oxidation to $6CO_2$ and $6H_2O$ as will $C_6H_{12}O_6$, though the weight of the former to the latter is as 84 to 180. But C_6H_{12} (hexylene) is not digestible in the animal system, whereas $C_6H_{12}O_6$ (glucose, fructose, galactose) is. Actually, of course, if we know the exact composition of a chemical compound, such as a carbohydrate, we can calculate the heat that can be obtained under ideal conditions. Except for a few substances, such as the sugars, most foodstuffs are not pure chemical substances, so that their maximum fuel value cannot be so calculated. Furthermore, the nitrogen of the proteins is not oxidized to, say, nitric acid in the animal body, but is excreted most frequently as urea [$CO(NH_2)_2$]. This compound thus removes nitrogen unoxidized and likewise takes with it carbon and hydrogen, both of which have heat values. Thus the theoretical amount of heat which can be obtained from a protein is much greater than that actually produced in the animal body.

A comparison of a carbohydrate like glucose, $C_6H_{12}O_6$, with a fat like tripalmitin, $C_{51}H_{98}O_6$, shows a much greater proportion of oxygen in the molecule of the former than in the latter, so that equal weights of each would give much more heat from the fat than from the carbohydrate.

394 Fuel Values versus Food Values

In burning foods by the method described above, actual heat values, called *fuel values*, are obtained under strictly controlled

conditions. But these values do not necessarily hold when food is oxidized slowly in the animal body. Here it must be noted that not all that is eaten gives rise to the amount of heat calculated from calorimetric experiments, and that the body loses heat in a great variety of ways, so that not all the heat obtained by the combustion of foods is actually turned into work. The body size and the kind of work being done are extremely important factors in deciding the relation between food intake and energy output. There is also the matter of excretion of nitrogen and hydrogen as urea, tending to lower the fuel value of proteins.

To gain sufficiently complete data on this subject numerous experiments have been conducted, mainly on the lower animals, but also on human subjects. These experiments have taken many forms, such as measuring the carbon dioxide evolved from the lungs during different kinds of activity, weighing the foods and the excreta, and even enclosing the subject of study in a huge calorimeter, in which every body activity could be observed. From these experiments conclusions have been reached regarding the importance of size, shape, sex, age, growth, mental and physical work and their bearing on energy requirements. These studies are classified under the heading *metabolism*, which includes all these changes dealing with the building up (*anabolism*) and the breaking down (*catabolism*) of living cells. The values obtained from such observations are more nearly the true, physiological ones and are called *food values.* Table 38 shows these two sets of values side by side.

TABLE 38

Heat Values of Foods in Calories per Gram of Food

Food	*Fuel Value*	*Food Value*
Carbohydrate	4.1	4.1
Fat	9.45	9.3
Protein	5.65	4.1

We must not suppose that the food eaten is immediately utilized as fuel. As we shall see later, carbohydrate and fat may go into storage in the body for use at some future date, and the protein may to some extent replace similar protein tissue in the body. Moreover, conditions may be very different in the fully grown adult from those in the growing child, who may be rapidly adding weight, and therefore not burning up all his fuel but storing it.

Most articles of diet are mixtures of two or more of the three basic foods. Thus beefsteak is somewhat more protein with a lesser quantity of fat, but contains no carbohydrate; plums and prunes are mainly carbohydrate with a small proportion of protein, though no fat. On the other hand, such common foods as milk, flour, beans, cabbage, lettuce, tomatoes, bananas and nuts are mixtures of all three classes. In the main, then, most foodstuffs are mixtures of all three, in, of course, different ratios. Tissues of animals, both land and water, contain no carbohydrate but are rich in fat and protein. The only foodstuffs containing only one of these three classes are refined sugars and extracted fats, for example, cane sugar and olive oil.

Though carbohydrates and fats may appear as storage in the body after digestion, fats contribute twice as much per unit weight to the energy intake as carbohydrates. Against this is the longer time of digestion required by fats—at least four hours as against three for carbohydrates.

Stress has been laid recently on the need for abnormally large quantities of fat in the diet of all who must live throughout the Arctic winter. To use carbohydrates with their smaller food value would require a tremendous intake of such foods, and there would appear to be a limit to which excess protein can be converted to fats. All this is not new of course, but since our operations in the Arctic and Antarctic have intensified in recent months more attention has been directed to dietary requirements in these regions.

395 Normal Energy Requirements

In general the average adult requires a minimum of 1800 Calories per diem merely to maintain life while in a position of complete rest; the same person at work of a light nature requires about 2700 Calories; whereas a lumberjack might require as much as 5000 Calories. Beyond the minimum stated above, the main cause of energy dissipation appears to be muscular activity.

During its period of growth the human body requires a gradually decreasing energy intake relative to body weight. Thus, whereas about 45 Calories per pound of body weight per diem is necessary up to the first year of life, this value falls to about 32 Calories at the age of ten, and to about 22 at twenty-one years. The energy intake of adults who have attained their full growth is regarded as being equal to their total energy output.

396 Essential Nature of Proteins

As energy producers, proteins are in the same class, weight for weight, as carbohydrates. On the other hand, fats and carbohydrates cannot be used to replace protein tissue in the body. Proteins, therefore, are an absolute requirement, with the other two of secondary importance. The amount of protein held to be necessary in the daily diet of an adult is between two and three ounces.

Most of the carbohydrates and fats which occur in common foods can be made available for use in the body, but a considerable difference exists among the proteins with respect to their value in the maintenance of life. Of the twenty-two amino acids known to occur in the proteins of food and of the body, ten have been shown to be essential constituents of the diet—the others it can construct for itself, given suitable sources of nitrogen. These ten include phenylalanine, lysine and tryptophane, proteins which do not include all ten are said to be incomplete and cannot by themselves maintain the structure of the body or even permit growth (§ 339).

397 Summary

Foods have two main functions: first to provide the daily requirement of bodily energy, and second to maintain the structure of the body.

The energy comes from the oxidation of certain foods, notably fats and carbohydrates. Proteins may also serve as fuel, but they are chiefly allotted to maintenance of the tissues.

The utilization of foods is accomplished by certain special organs with the aid of very small quantities of inorganic substances, of enzymes and of specific organic compounds called vitamins.

Foods which serve as fuel may have their fuel or calorific values determined both chemically and physiologically, and there is fair agreement between these two sets of values. These foods are actually burned (slowly, of course) within the body. The oxygen enters through the lungs and carbon dioxide and water are expelled; carbon dioxide leaves by the lungs, and water by the lungs, the pores and the excreta.

Most foods are mixtures of some or most of the above components. But some foods are richer in essentials than others.

Fats have about twice the fuel value of carbohydrates and are of particular importance in cold climates.

Growing children require a relatively larger proportion of food than adults, particularly for growth and for maintenance. They need calcium and phosphorus in particular, since the bony skeleton and teeth are dependent on these two elements for their proper development.

Questions

1. What is the main sustenance of a nomadic tribe?
2. What three classes of foods represent the bulk of ordinary diets?
3. What are the functions of a food?
4. To what extent may the human body be considered a furnace?
5. Distinguish carefully between fuel value and food value. How may each be determined?
6. Why are proteins the most important of the three classes of foodstuffs?
7. Write a paragraph on pemmican, discussing its value as food.

28

Digestion and Assimilation

398 Definitions

The term *digestion*, as it will be used here, may be defined as the act of changing food of various kinds into such substances as may be absorbed by the body, either for the provision of the energy required by the human machine or for the maintenance and repair of the machine itself. By comparison, the *assimilation* of food is the absorption of the digested food by the appropriate organs for incorporation into the types of chemical substances characteristic of the body.

Since most foods are solids and must be absorbed as liquids, digestion is carried on in aqueous solution and by means of chemical reagents dissolved or colloidally suspended in water. In this connection a distinction must be drawn between the chemical reagents used in the glass, porcelain and metallic apparatus of a chemical laboratory and those suited to the kind of containers that compose the alimentary tract. The dextrinization of starch and its hydrolysis (as well as that of the disaccharides) with the ultimate formation of glucose, etc., may be effected chemically in vitro by boiling with water to which a little of a strong acid (HCl) has been added. A similar procedure is employed for changing a complex protein into its simpler constituent amino acids, and fats undergo hydrolysis on boiling with relatively large quantities of an alkali such as sodium hydroxide. Each of these three types of compounds, therefore, undergoes hydrolysis by the use of corrosive chemical substances at a temperature fatal to animal tissues. But in the digestive tract exactly similar hydrolyses occur but at body temperature (98°F or 37°C) and by the aid of very mild reagents, if we except the 0.4 per cent hydrochloric acid content of the stomach. These reagents are called *enzymes* (Greek, *in leaven*), since several of them are found in yeast.

399 Enzymes

Enzymes are protein-like bodies produced by living organisms in their life cycle (for example, yeast cells) and, though themselves inanimate, are subject to somewhat the same limits and conditions of existence as the organisms which produce them. Thus they may be active in an acid but not in an alkaline medium, or vice versa; they are also destroyed by heat. Except in this latter respect they resemble inorganic catalysts in many ways, and in some ways they simulate the actions of bacteria. At any rate they are the catalysts of living cells, and very selective in their action.

Some enzymes are concerned with alcoholic fermentation, the production of acetic acid from ethyl alcohol and many other processes. Those in the digestive tract, however, chiefly bring about hydrolysis and are therefore called *hydrolytic*. They may be classified as (1) proteases, protein splitting; (2) lipases, fat splitting; (3) amylases, starch and sugar splitting. Table 39 summarizes the commoner enzymes with their sources and actions.

TABLE 39

THE COMMON DIGESTIVE ENZYMES—THEIR SOURCE AND ACTION

Class of Enzyme	Name of Enzyme	Source	Action
	Amylopsin	Pancreatic juice	Starch to maltose
	Lactase	Intestinal juice	Lactose to glucose and galactose
Amylases	Maltase	Intestinal juice	Maltose to glucose
	Ptyalin	Saliva	Starch to maltose
	Sucrase (or Invertase)	Intestinal juice	Sucrose to glucose and fructose
Lipases	Lipase	Gastric and pancreatic juices	Fats to glycerol and fat acids
Proteases	Erepsin	Intestinal juice	Peptones to amino acids
	Pepsin	Gastric juice	Proteins to proteoses and peptones
	Trypsin	Pancreatic juice	Proteins to amino acids

400 Organs of Digestion

The organs of the body which are directly concerned with the digestion of food are, in order, the mouth, the stomach, the little intestine, the pancreas and the gall bladder; they constitute the alimentary tract. In addition to them, the blood and the lymphatic systems carry the digested foods to the liver and to dis-

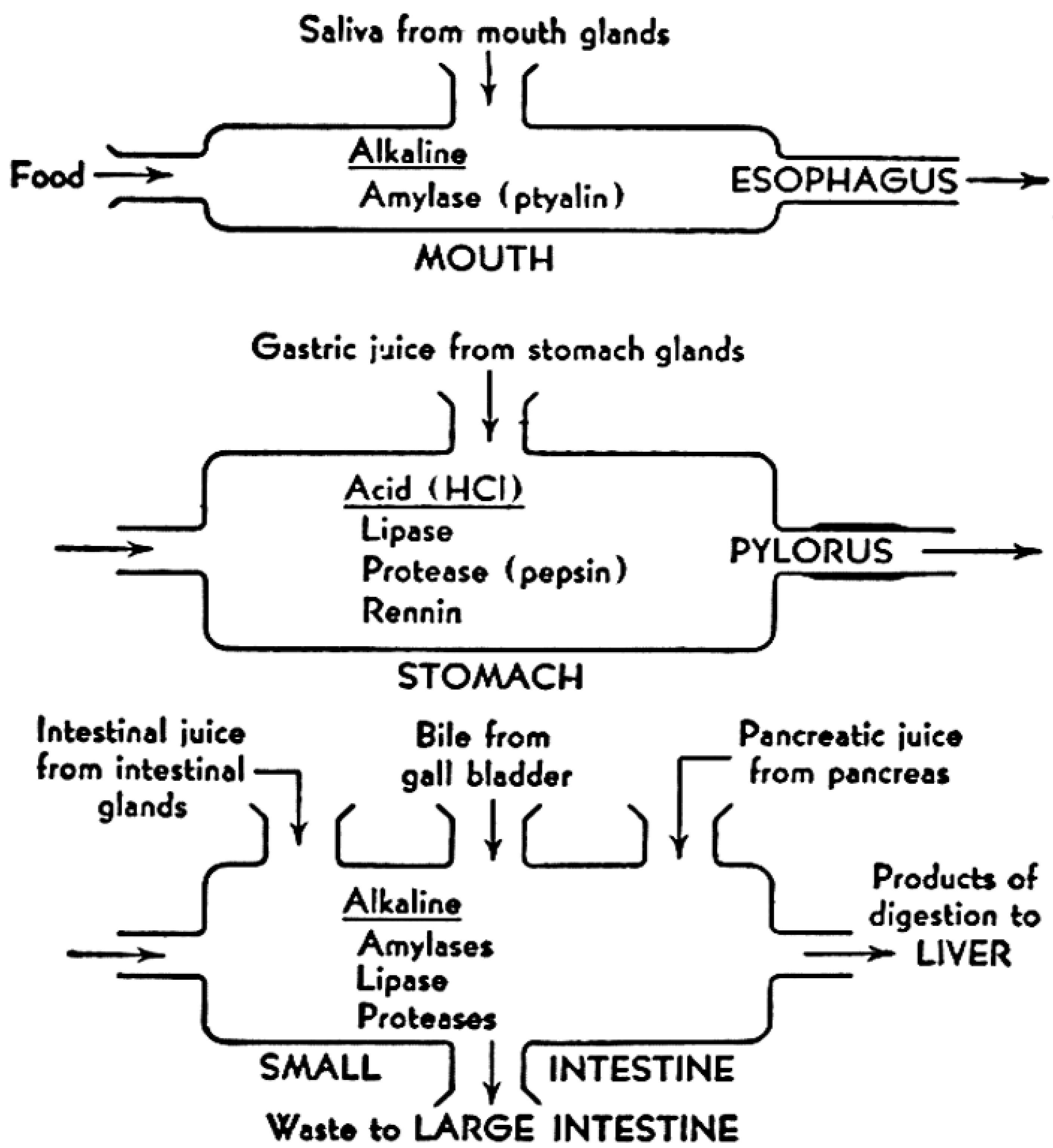


FIG. 70. Diagrammatic representation of the digestive tract and its equipment.

tribute them to appropriate parts of the body. Figure 70 is a diagrammatic representation of the main organs concerned with digestion. Each organ is named here, its condition of acidity or alkalinity stated and its content of digestive factors indicated.

The sketch, though of course diagrammatic, will serve to simplify the description of the digestive process. The various enzymes listed in different parts of this sketch are active only under the condition of acidity or alkalinity characteristic of the organ in which they occur. Thus ptyalin, beginning the hydrolysis of starch in the mouth, will not perform this function in the stomach when it

becomes sufficiently acid; contrariwise, pepsin requires an acid medium.

401 The Functions of These Organs and the Fate of the Foods

(1) *The Mouth.* The function of the teeth is to grind up solid matter into smaller particles, so that the particles, because of their large surface, may be more readily attacked by the digestive juices. The only foods to begin digestion in the mouth are starchy ones, like bread and cereals which are attacked by ptyalin in the saliva. The act of swallowing moves the food, impregnated with lubricating saliva, downward into the stomach, where for a while, until acidity increases, the starches continue to be hydrolyzed.

(2) *The Stomach.* This organ has a variety of functions, one being to act as temporary storage for swallowed food, and another to churn up the food to a consistency suitable for passing on to the little intestine. From the stomach walls are secreted hydrochloric acid and the enzymes lipase, pepsin and rennin, these constituting the gastric juice. Here begins the hydrolysis of the fats and proteins, though it is not by any means completed at this stage. When the acidity of the stomach contents reaches a definite value, the pylorus, the muscle-bearing tube leading into the little intestine, opens and allows the chyme to flow slowly onwards. The stomach movements have a great bearing on the quality of the chyme, and the flow of food onwards is maintained by that continuous movement of the digestive tract known as *peristalsis*.

(3) *The Little Intestine.* This is the organ which completes the process of digestion. It receives from its own glands the intestinal juice, from the pancreas the pancreatic juice and from the gall bladder a small quantity of bile. The medium here is alkaline, and these juices contain the enzymes necessary to change all carbohydrates to glucose, fats to glycerol and fat acids, and proteins to the simpler amino acids. The function of the bile is to aid in emulsifying the fats so that saponification may proceed more rapidly. The products of digestion go to the liver, while unwanted or excess products pass into the large intestine, whose main function is their excretion.

Later the carbohydrates may be burned to supply heat energy or be stored in the liver and muscles as glycogen, the energy reserve compound of animals. Glycerol and the fat acids may be

burned for the same purpose and also synthesized into the appropriate body fats, to provide a protective coating for the tissues and be available for energy when required. The amino acids may likewise be burned or also synthesized into the protein tissues of the body. Thus, though eating and digestion are intermittent processes, the burning of food fuels and the replacement of energy stores and tissues go on more or less continuously.

This in outline is the fate of the three bulk foods of the normal diet. Without them there is no provision of energy and no replacement of worn-out tissues. These foods, however, are dependent for their digestion, assimilation and use on the inorganic salts.

402 Inorganic Salts

These salts are required for two reasons: first to replace the loss by excretion, and second to regulate the very necessary conditions of acidity and alkalinity not only of the digestive tract but of the entire system as well. They form but a small proportion of the diet and are of inorganic origin whether they are absorbed from meat, vegetables or fruit. Purely carnivorous animals like the lion and tiger get all they require from the animals on which they feed. These inorganic salts consist mainly of the chlorides, phosphates and iodides of calcium, iron, magnesium, manganese, potassium and sodium, and constitute about 4 per cent of body weight, the rest being oxygen, carbon, hydrogen, nitrogen and sulfur. From the point of view of quantity, calcium is the most important of these elements, accounting for about 1.5 of the 4 per cent; this will be apparent from a consideration of the large mass of the skeleton which is mainly calcium phosphate. Phosphorus is next, about 1.0, leaving 1.5 to include all the others. Calcium and phosphorus are found in many foods—indeed in most foods—but nowhere are they of such importance as in milk and cheese. Expressed in parts per hundred thousand of edible food, milk contains 120, cheese 930 and egg yolk 130 parts of calcium. Phosphorus in the same foods is present to the extent of 90, 680 and 520 parts, respectively. Egg yolk and beef are the best sources of iron.

These elements are found combined in the body, therefore, mainly with two functions, to form the skeleton and teeth and to act as soluble salts in body fluids. The commonest salt is sodium chloride, which is responsible for hydrochloric acid of the gastric

juice and largely connected with the retention of body fluids in the tissues.

The average daily amount of these salts excreted by an adult is about two ounces, or one twelfth of 1 per cent of body weight. Though this may appear a small amount, bodily functions are impossible without it. Iron possesses considerable significance in that it is an essential component of hemoglobin, though present to the extent of only 0.47 per cent. Iodine is found combined in thyroxin, a product of the thyroid gland, which has such an important influence on the whole system. Though a wide variation occurs in the iodine content of different foods, depending, in the case of grains and fruits, on the proximity of salt water, the following figures give an approximate idea of the amount of iodine present in parts per billion in some common foods: barley, 73; carrots, 170; corn, 52; goat's milk, 400; oats, 175; salmon, 45 to 324; wheat, 4 to 10.

These values are not exhaustive, but represent the highest so far obtained. In goitrous regions, where foods show an abnormally low iodine content, iodine deficiency may be corrected by the use of iodized salt in cooking and seasoning, though this may be undesirable when goiter has already developed.

403 The Vitamins

The digestion and assimilation of foods utilize carbohydrates, fats and proteins. They are hydrolyzed and, unless put into storage as fat and body tissue, are oxidized in aqueous solution at a temperature of 37°C to produce the energy that is required each day. This series of processes is carefully controlled by numerous agents, among which are the inorganic salts, numerous enzymes and vitamins. Only within the last thirty years has attention been drawn to the necessity of vitamins to the general well-being of the body.

Though the discovery of the vitamins is a recent achievement, it had long been recognized that sailors on long voyages were susceptible to attacks of scurvy if their diet lacked fresh fruit and vegetables, notably the citrous fruits. This and many other examples led to the belief that disease could be the result of diet deficiencies. Undoubtedly the small quantities of these vitamins available contributed to the difficulty of their identification.

Extensive experiments on the isolation and synthesis of these substances have produced valuable information as to their source, usefulness and chemical structure.

For convenience, the vitamins are listed alphabetically: A, B, C, D, E and K. Though only one compound has so far been listed for A, one for C, one for D, one for E and one for K, under the heading of B some twelve are known at the present time. The vitamins have been divided into two main classes: (1) *fat-soluble,* A and D, and (2) *water-soluble,* B, C, E and K. This classification gives a clue to the place of their occurrence, for example, A and D in fish liver oil and C in fruits. In Table 40 the names of the known vitamins are listed, together with their alphabetical titles, and their known function in animal health. Under the heading chemical relationship are the names of some compounds whose chemical structure has already appeared in Part 2; the actual formulae are beyond the scope of this text.

TABLE 40

THE VITAMINS

Name	*Function*	*Chemical Relationship*
A—Axerophthol	Anti-xerophthalmic	Cyclohexane
B_1—Thiamin	Anti-neuritic	The pseudo-alkaloids
B_2(G)—Riboflavin	Aids growth	Quinoline
Niacin, nicotinic acid	Anti-pellagra	Pyridine
B_6—Pyridoxine	Anti-dermatitis	Pyridine
Pantothenic acid	Anti-dermatitis	Propionic acid
Biotin	Aids yeast growth	Thiophene
p-Aminobenzoic acid	Anti-gray hair	Benzoic acid
Inositol	Anti-baldness; aids growth	Cyclohexane
Choline	Prevents shortening and thickening of bones in the young	Trimethylamine
Folic acid	Aids growth	Unknown
C—Ascorbic acid, cevitamic acid	Anti-scorbutic	Glucose
D—Calciferol	Anti-rachitic	Phenanthrene
E—Tocopherol	Anti-sterility	Hydroquinone
K	Aids blood clotting	Quinone

The absence of vitamin A delays growth and causes the appearance of eye diseases (night blindness, for instance), which are but concomitants of weakening of body vigor and susceptibility to infection. Its presence is of greatest importance to health. It is found in largest quantities in milk, butter, egg yolk, cod liver oil; to a smaller degree in animal fat and generally in the green

leaves and embryos of many seeds. It is found also in many roots, such as carrots.

The B vitamins are very widely distributed in nature, being found in liver, yeast and grains. The nucleus of the wheat grain is rich in many of these, as well as in vitamin E. The absence of the B vitamins is generally associated with disorders of the nervous system.

Commonly found in much greater quantity than any of the others, vitamin C occurs in many fruits, such as oranges, lemons, tomatoes, raw onions and potatoes; but there is very little in milk or eggs. It is destroyed by excessive heating in air. A common symptom of vitamin C deficiency is scurvy, and its presence is necessary to the healthy condition of the blood capillaries.

Vitamin D occurs associated with A in animal oils. The alcohol (sterol) ergosterol may be synthesized chemically, and, if irradiated with ultraviolet light, behaves as the naturally occurring vitamin. It is essential particularly to the building and maintenance of bones and teeth, as it assists in the assimilation of calcium and phosphorus. Its deficiency is indicated by imperfect bone and tooth structure, especially in the young. The chemical structure of calciferol is very similar to that of the sex hormones, those subtle compounds which seem to control not merely sex but most of the characteristics which distinguish man from vegetables.

404 Vitamins Are Not Drugs

These vitamins, produced in the animal and vegetable kingdoms, should of course be present in the diet in order to exclude the possibility of such diseases as appear in their absence. That they are presumably not synthesized in the human body makes their inclusion in the diet of the greatest importance. Their quantity does not appear to be important, since the proportion of vitamins required, compared with the mass of food either taken or needed, is extremely small, thus demonstrating the catalytic nature of these substances. Vitamins, moreover, should not be regarded as medicinal substances so much as food requirements. Nevertheless, vitamin deficiency over an extended period requires special treatment involving larger amounts of the necessary substances than would normally be required; hence the necessity of reinforcing an inadequate diet by concentrated extracts of the vitamins.

This reinforcement is necessary also in the treatment of almost all diseases, not merely those indicated above. Moreover, the presence of vitamins is a kind of guarantee against infection generally. It is likewise important that during pregnancy and lactation the diet should be increased with respect to its content of protein, inorganic salts and vitamins.

Table 41 shows the quantities of certain vitamins required by an adult. They are expressed, in some instances, according to a system that is not related to weight but to the physiological effects as demonstrated by experiment—international units, so-called. In the third column are certain common sources of the vitamins, together with the amounts equivalent to the values of the second column.

TABLE 41

CERTAIN VITAMINS—THEIR REQUIREMENTS AND SOURCES

Vitamin	*Adult Requirement*	*Source and Quantity*
A	3000 units	Cod liver oil, 15 to 45 drops
		Carrots, 4 ounces
		Whole wheat flour, 21 ounces
		Spinach, 1 ounce
		Milk, $\frac{1}{3}$ to 1 cupful
		Butter, 5 ounces
		Calf's liver, $\frac{1}{9}$ ounce
B_1 and B_2	500 units	Whole wheat bread, 18 ounces
		Potato or meat, $2\frac{2}{3}$ pounds
		Milk, $3\frac{1}{2}$ pints
		Liver, 11 ounces
		Dried brewer's yeast, $\frac{2}{3}$ ounce
		Egg yolk, 18 ounces
C	30 milligrams	Lemon or orange juice, $\frac{1}{5}$ ounce
		Potato, 7 ounces
		Milk, $2\frac{3}{5}$ pints
		Liver, 6 ounces
D	500 units (for a child or during pregnancy)	Cod liver oil, 80 drops
		Milk, 22 quarts
		Butter, 54 ounces
		Egg yolk, 7 ounces

405 Protective Foods

In the previous pages we have considered food requirements in this order: bulk foodstuffs, inorganic salts, vitamins. This order

is the one most familiar to us in our history. But from the point of view of what is essential, first, to our survival and, second, to our comfort, the reverse order is the realistic one. Without vitamins we begin to cease to function. Furthermore, even with vitamins and with plenty of bulk foods, digestion and assimilation do not take place if our diet lacks inorganic salts.

Of recent years the idea of a "protective diet" has developed. Such a diet must contain all the vitamins and inorganic salts and must include all those essential foods which can be counted on to supply them as well as the necessary amino acids derived from proteins. Carbohydrates and fats then become supplementary foods to supply the energy required for the different demands of living. The "protective foods" include milk and milk products, eggs and fruits first of all; to them are added other foods known to contain iron and iodine. This scheme for diet places the responsibility for health on the vitamins and inorganic salts, leaving the bulk foods to the discretion of the consumer.

406 Summary

Digestion is the preparation of eaten food by the alimentary tract so that it may be absorbed or assimilated into the body to serve as fuel or as tissues characteristic of the body.

The organs of digestion are the mouth, the stomach and the little intestine. Associated with the little intestine are the gall bladder and the pancreas.

Digestion is effected in these organs by fluids which are aqueous solutions containing enzymes, hydrochloric acid (in the stomach) and inorganic salts.

These enzymes are colloidal, protein-like bodies, easily destroyed by excess heat, and capable of splitting carbohydrates, fats and proteins into their simpler components. This splitting is, in effect, hydrolysis. Starch and sucrose, for example, give monosaccharides under this treatment; fats give glycerol and fat acids; proteins are broken down into their constituent amino acids (§ 339).

Inorganic salts provide not merely the correct acidity or alkalinity of the organs of digestion but also enter into the bodily structure; hence the necessity of calcium, phosphorus, iodine and iron in particular.

Governing these processes and preventing diseases which occur in their absence are the vitamins. Those so far discovered have been shown to be absolutely necessary to the well-being of the body. Without them the bulk foods are of little value. In consequence, more and more stress is laid on those foods rich in vitamins, as milk, eggs, cheese, butter and fruits.

Protective foods are those which contain an adequate supply of essential vitamins, inorganic salts and proteins, notably milk, eggs and fruits.

Questions

1. What do you understand by the terms digestion and assimilation?
2. What organs compose the digestive tract?
3. The digestion of food is largely a hydrolytic process. Explain this statement.
4. What are enzymes? How may they be classified? How does each class function?
5. Trace the digestion of (*a*) carbohydrates, (*b*) fats and (*c*) proteins in the alimentary tract, indicating the function of the various digestive fluids, their sources and enzyme content.
6. What roles do acidity and alkalinity play in digestion?
7. What are the inorganic elements essential to life?
8. What are vitamins? How is each named, and what is its individual function?
9. Name the classes of foods in order of their essential importance.
10. Discuss protective foods.

29

Some Common Foods and Their Importance

407 Food Value and Its Limitations

In the two previous chapters attention was drawn to the classification of foods, the organs concerned with their digestion and assimilation, the mechanism of digestion, the value of food in terms of available energy and the interdependence of dietary components. It is now possible to consider what is meant by the term *food value.* What has been described as the fuel values of foods may be accepted as a scientific basis on which to build the conception of food values. The body requires a minimum of energy on which the bare maintenance of life depends, and this may be expressed appropriately in calories, the common unit of energy. But the utilization of this energy available from the various foods usually eaten depends upon the degree to which digestion and assimilation take place; and they in turn are dependent upon a sufficient supply of inorganic salts and of vitamins, the last two being scarcely expressible in terms of heat. Here the strictly scientific statement that 1 gram of carbohydrate may on oxidation yield 4.1 Calories is limited by the extent to which this potential energy of the carbohydrate is actually utilized in the animal economy. Thus the heat values attached to articles of diet may be very illusory and may, of course, be absolutely false if it is found that any one person is unable to utilize such foods. Moreover, it is conceivable that we may consume a huge amount of one article of diet (perhaps sufficient in calorific value to suffice for several meals), but only a small proportion of this food may be digested. In addition, the excess may produce a positive dislike for any more of it again.

The psychological aspects of taste, of preparation, of serving, etc., may also act as a deterrent to digestion. They must not be

overlooked, for the sources of supply of the digestive juices may fail to respond adequately if the necessary stimulus is lacking. This fact calls to mind such expressions as "one man's meat" and "another man's poison," as well as the familiar "mouth-watering" —all phenomena having their basis in fact. These observations tend to qualify the exactness with which fuel values may be considered as food values.

408 Natural Feeding

Fortunately for all of us, nature begins our feeding with materials not too foreign to our prenatal mode of sustenance, and also provides us all through life with foods that are, in the vast majority of cases, mixtures of the different and essential constituents. Even in the simplest foods we encounter a diversity of constituents in conformity with our requirements. Our earliest food, milk, is perhaps the most diverse of all, and its animal origin is matched by eggs—these two constituting two of our most valuable foods from almost every aspect. If to these we add whole grains, such as wheat or oats which have not suffered too much refining, our trio contains two important embryos of potential life. And if these are regarded as self-sufficient in themselves, they should contain all vital essentials and in consequence serve as most valuable articles of diet for man. They have been for many generations and will no doubt continue to be.

409 Milk

Whether obtained from the cow, goat, sheep or camel, milk is the commonest of all human foods; and in some parts of the world it, or its products, is a much more fundamental constituent of the diet than on this continent. Of recent years we have come to realize its dietary importance and to understand why nomadic peoples relied so on their milk-giving animals. Moreover, there is no other single foodstuff which is so subjected to processing. Milk products include cream, butter, cheese, buttermilk, fermented milk, evaporated, condensed and powdered milks and ice cream. Surplus milk supplies, moreover, may be utilized to prepare anything from chicken feed to lacquers and buttons.

The approximate percentage composition of cow's milk is carbohydrate 5, fat 4.0, protein 3.4, inorganic salts 1 and water 86.6. Goat's milk is much richer in fat, and sheep's milk is richer in both

fat and protein. Human milk, on the other hand, is much poorer in fat and protein and richer in carbohydrate. Under the heading of inorganic salts, all milks contain considerable quantities of calcium and phosphorus but are a very poor source of iron. They are quite high in content of vitamins A and B, with much less D and undependable traces of C. Quite apart from this scientific analysis, milk is a perfect food for a young mammal for a considerable period in the early part of its life. So seriously do civilized communities regard the importance of cow's milk that its production, processing and distribution are the subject of close governmental supervision. More recently the tuberculin testing of cows, with consequent destruction of infected animals, has safeguarded its source of production; and pasteurization is commonly enforced in all towns and cities where milk cannot be delivered within a few hours of its removal from the cow.

410 Pasteurization of Milk

Owing to a variety of circumstances any milk is extremely likely to contain a small amount of pathogenic bacteria (of the so-called *B. coli* group) in addition to those organisms concerned with fermentation, which, if anything, are beneficial in their ability to render milk digestible. The object of pasteurization is to destroy the former and conserve the latter along with the vitamins and, in addition, to preserve the flavor and texture of the milk. Since the effectiveness of pasteurization is largely dependent upon the temperature and mode of handling, the commonest procedure is, after straining, to heat the milk rapidly up to 148°F, keep it there for a minute and then cool it rapidly to 38°F, when it is bottled. This procedure reduces the pathogenic bacteria to a minimum while retaining the milk in practically the same colloidal condition as when it came from the cow. Thus in time the cream tends to separate towards the top of the container where it becomes visible. Pasteurization may destroy a fraction of the little vitamin C present but otherwise hardly affects the food value.

Mechanical treatment of whole milk can give rise to a product which is whiter in color and from which the cream does not separate so readily. This is called *homogenized* milk, and should be somewhat more readily digested than ordinary milk because of the fine state of division of the suspended particles of fat and protein.

Milk is a natural colloidal solution, where in the dispersion me-

dium we find solid casein and the semi-solid fat forming a complex emulsoid-suspensoid. In addition there is a small fractional percentage of protective colloid (albumin), which prevents a too early separation and coagulation of the dispersed phases. Fortunately for the young child, human milk contains more of this albumin than cow's milk, thus accounting for the more desirable breast feeding for infants.

It is interesting to note that a human infant doubles its weight in 6 months, a calf in about 6 weeks and a baby rabbit in about 6 days; hence rabbit's milk is richer than cow's milk and far richer than human milk in the tissue-building constituents, such as protein and calcium.

411 Cream

Centrifuging milk in the ordinary cream separator rapidly separates the butterfat and some of the casein from the rest of the milk, the degree of richness of the cream so produced being proportional to the rapidity of centrifuging. Various grades of cream are supplied to the market, ranging in butterfat from 15 to 40 per cent, the higher percentages being commonly used for whipping. The separated milk may be fed to farm animals, and contains most of the lactose, some vitamin B_1 and B_2 and much of the inorganic salts. Devonshire cream is produced by allowing cream to rise to the surface of heated milk; it is very rich and thick.

412 Butter

Rapid mechanical agitation of cream causes coagulation of the butterfat. This agitation is more effective when the cream is slightly sour. Butter, except for a legally defined percentage of water, is a mixture of the glycerides of many fatty acids from butyric (with four carbon atoms) up to stearic (with eighteen); it also contains much of the original content of the fat-soluble vitamin A present in the original milk. We find, left behind in butter manufacture, buttermilk, a rich colloidal solution of protein, lactic acid and inorganic salts. This protein is casein, the chief nitrogenous constituent of milk.

413 Margarine

This is a butter substitute in which fats of vegetable or animal origin (or both) are incorporated with whole milk and so treated

as to give the finished product the natural flavor of butter. Of course margarine is (or should be) cheaper than cow's butter; otherwise there would be no reason for its manufacture. If its manufacture is as well supervised as the manufacture of butter, however, there is no need to regard it in the same way as we tend to regard adulterated products generally. Ordinary butter always shows a trace of acidity, rather more than usual giving it the undesirable rancidity attributable to butyric acid. On the other hand, carefully prepared margarine has a lower acid value and will keep better; it is also less volatile and so more nearly approaches lard for cooking purposes.

414 Cheese

Cheese is a name used to cover a great variety of foods containing largely the protein of milk, or casein. It may be made from whole milk, partly skimmed or separated milk, or from completely skimmed milk. By the action of rennet, which contains the coagulating enzyme rennin, a curd is produced in each instance. When whole milk is used, the cheese produced is known as Cheddar after it has been allowed to ripen; this is the commonest type of cheese. Limburger is in the same class, though ripened by a different process; in this class are likewise Stilton, Neufchâtel and Gorgonzola, each with its characteristic process of ripening. Roquefort is made chiefly from the whole milk of sheep; cream cheese is Neufchâtel with added cream. All these varieties contain not less than 30 per cent of butterfat, over 20 per cent casein and much calcium.

Edam, Swiss and Camembert cheese are made from whole or partly skimmed milk and contain 20 to 30 per cent of butterfat. Cottage cheese contains about 2 per cent butterfat, being thus mostly protein.

Soft cheese contains a larger proportion of water than a hard or pressed cheese. In the manufacture of any cheese, the precipitated curd is relatively indigestible. During ripening, by the aid of different molds, a characteristic flavor is produced along with a very digestible product. Cheese is one of the richest of all processed foods.

In eastern Europe and Asia Minor milk, fermented by specially chosen enzymes, closely resembles buttermilk and is a common article of the diet. For many centuries, indeed, a favorite drink of

the Arabs has been fermented mare's milk, but this type of food is indigenous to the East.

Of late years experiments conducted aimed at increasing the vitamin D content of milk have met with considerable success. Except for the low content of this vitamin as well as of C, and except for a smaller percentage of iron than is normally required by the human species, milk may be said to be a perfect food for the young. The adult requires in addition some roughage, but this may easily be obtained from the other materials ordinarily eaten without the necessity of making a special effort to have it.

415 Eggs

Next in order of importance are eggs, the richest of natural foods—obviously so since they represent all the factors for the new bird life, from the embryo onward. Of the two parts of the egg, most of the food value is concentrated in the yoke. Thus the white of the egg contains nearly twice as much water as the yoke, about three fourths as much protein and scarcely any fat, whereas nearly one third of the yoke is fat. The whole egg is especially rich in protein, fat, calcium, phosphorus and iron, though lacking in carbohydrate.

One advantage that milk and eggs in particular possess over most foods is that they contain the very necessary amino acids lysine, histidine, arginine, tryptophane, etc., without which complete replacement of worn-out protein tissue is not readily effected (§ 339). Like any particularly rich natural foodstuff, eggs are susceptible to a decomposition which makes them highly unpalatable; this decomposition is readily evidenced by the evolution of hydrogen sulfide. To guard the purchaser against such eggs, special precautions have to be taken which in most cases are none too effective. Two methods have been devised for overcoming the difficulty of keeping eggs fresh. One consists of breaking and drying the contents in such a manner as to produce a fine powder much favored by industrial users of eggs; the other consists of breaking and then freezing the contents, either separately or combined. This second method requires a low temperature both for freezing and for storing, but the results have been most satisfactory.

416 The Grains

They form a large proportion of any diet, whether in the form of breakfast foods, bread, biscuits, cake or pastry. In their original

form these grains consist of three parts: (1) the inner germ (or embryo of the new plant), which approximates 2 per cent of the whole grain and contains fat, protein and certain vitamins such as B and E; (2) the endosperm, composing eight to nine tenths of the whole grain and containing starch and gluten, but deficient in vitamins; and (3) several cellulosic layers or coverings, commonly termed bran (here occurs a little protein with very little fat, but with most of the inorganic salts). In reports dealing with the analysis of foods the term *crude fiber* represents indigestible cellulose, and *ash* may be taken as a measure of the content of inorganic salts.

Oatmeal is somewhat richer in calcium than barley, though their content of phosphorus and iron is about the same. Whole wheat

	BARLEY	CORN MEAL	OATMEAL	RICE	RYE FLOUR	WHEAT (Whole)	WHEAT (Fine)
Protein	10.6	9.2	11.9	8.0	6.8	11.7	12.6
Fat	4.2	1.9	8.6	0.3	0.9	2.0	1.7
Carbohydrate	66.3	75.4	70.0	79.0	78.7	71.9	73.1
Calcium	0.043	0.018	0.069	0.009	0.018	0.031	0.020
Phosphorus	0.400	0.190	0.392	0.096	0.289	0.238	0.092
Iron	0.004	0.001	0.004	0.001	0.001	0.0025	0.001

FIG. 71. Percentage composition of the grains.

contains nearly three times as much phosphorus as white flour. Whole wheat also contains all the constituents of the clean grain. Fine wheat is the milled grain freed from the bran and part of the germ, the germ giving rise in time to an unsatisfactory flavor. Unfortunately the refining leads to loss of valuable vitamins, especially B. During World War II an additional amount of thiamin was added to wheat flour for bread making, bringing the content up to dietary standards. Wheat flour is the greatest food commodity in the international market. Though in certain respects inferior to barley and oats, wheat nevertheless contains more gluten than any other of the common grains. It is this gluten which, in the presence of water, binds the grains of starch together to give a satisfactory product during cooking.

Corn spoils readily because of its high content of fat. Its use today is chiefly for the production of glucose syrups and of alcohol. Moreover, diets in which corn bulks too large tend to permit pellagra, for lack of nicotinic acid.

Oats are used chiefly for the preparation of oatmeal and rolled oats and as a valuable horse feed. In making oatmeal cakes, oatmeal must be mixed with wheat to give it the necessary binding effect.

Rye is very widely used in northern Europe in making bread, but is not popular elsewhere. It is, however, much superior to corn in dietary constituents, and ranks above wheat except in gluten content.

Rice requires more moisture for its cultivation than any other grain and is the food of fully a third of the human race. It is cultivated most extensively in India and China, and to a small extent on this continent. "Polished" rice is deficient in B and if largely consumed causes beriberi. The vitamin is present in the discarded husks.

Barley formed the staple grain of the ancient Egyptians and is the richest of all grains in calcium, phosphorus and iron. It is much favored as a food for infants and invalids. Its gluten content is low; but, when mixed with much wheat flour, it forms a very satisfactory flour for baking purposes. The chief use of barley, however, is in the manufacture of ethyl alcohol by a fermentative process.

The proteins of grains are not so good as those of milk, eggs and meat; and grains alone may be a very unsatisfactory diet, being deficient in certain salts and (especially with modern refining methods) vitamins. Fruits, potatoes and, to a less extent, meats are sources of vitamin C. Grains are chiefly energy producers because of their high carbohydrate content. Their low vitamin content compared with their fuel value definitely requires that they be supplemented by other foods richer in vitamin and high-grade protein.

417 Meats and Fish

Meats and fish vary in texture, fat content and palatability, but the fatless, edible portions (that is, excluding bone, entrails, etc.) are approximately 70 per cent water by weight when raw.

Meat may be chosen to include or exclude most of the fat, some being naturally fatter than others, for example, pork as compared with chicken. In fish, on the other hand, the fat is usually interspersed with the lean so that the choice has to be made rather with respect to the kind of fish than to the cut. Thus salmon may con-

tain as high as 13 per cent fat and cod as little as 0.2 per cent. Since the fats of domestic animals contain practically the same fatty acids as human fat, it follows that they are much more likely to be palatable than the fats of fish, whose content of unsaturated fatty acids is quite high. On the other hand, it is probably important that the food should contain some highly unsaturated fat acids. Thus the solid or semi-solid fats of domestic animals contain much palmitin, stearin and olein, which are relatively odorless, whereas the higly unsaturated acids found combined in fish oils have considerable odor, which some find distasteful.

Cured meats and fish lose water during the processes of smoking, etc., and so the protein and fat percentages are always higher than in the same foods when raw and uncured. As regards inorganic salt content, fish on the average are richer in calcium and phosphorus, though poorer in iron, than the flesh of land animals. Incidentally, the blood of crustaceans, such as the lobster, contains copper instead of the iron so characteristic of animals with red blood. In Table 42 are shown some values which may be of interest in considering the composition of these foods.

418 Vegetables

Though vegetables have always to some extent formed part of the human diet, during the past decade improved methods of agriculture and better transportation facilities have created a greater demand than formerly for fresh farm produce of all kinds. Originally, the *canning* process preserved cooked meats and condensed milk. It was extended to fruits and vegetables, both cooked. In order to meet the demands of foreign consumers and to conserve shipping space, scientific desiccation replaced the older sun-drying methods. Slow freezing of all fresh foods is frequently destructive of both texture and flavor. But rapid freezing at a very low temperature has now made available, even to consumers at a great distance, such different foods as fish, peas and strawberries. Their retention of both texture and flavor is truly remarkable.

419 Potatoes

Next to the grains, potatoes are the most important and abundantly cultivated of all vegetables. In some countries potatoes may form the chief source of starchy foods, whose failure in any

TABLE 42

THE COMPOSITION OF FOODS*

(All data refer to edible portion. They show energy value in Calories, and constituents in grams, or in the case of iron in milligrams, per 100 grams.)

Food	Calories	Protein	Carbo-hydrate	Fat	Calcium	Phos-phorus	Total Iron	Percentage Waste
Almond nut	657	18.8	16.0	55.3	0.239	0.465	4.54	—
Apple	47	0.3	10.8	0.2	0.007	0.012	0.23	9
Bacon	550	9.0	—	55.2	0.010	0.096	2.50	5
Barley (meal)	354	10.6	66.3	4.2	0.043	0.400	4.10	—
Beef (sirloin)	381	12.9	—	35.3	0.007	0.139	3.54	15
Butter	772	0.2	—	83.0	0.015	0.017	0.20	—
Cabbage	42	1.3	8.7	0.1	0.045	0.029	0.98	30
Cheese (skimmed)	194	33.0	3.0	5.0	0.931	0.683	1.30	—
Cheese (cream)	549	5.3	1.3	56.1	0.635	0.528	1.30	—
Chocolate	554	4.8	59.9	31.1	0.092	0.455	3.28	—
Cornflour	363	0.8	87.6	0.1	0.018	0.190	0.90	—
Cream	215	3.0	4.0	20.0	0.110	0.090	0.11	—
Egg	160	12.4	0.7	11.5	0.067	0.180	2.50	12
Flour (whole wheat)	361	11.7	71.9	2.0	0.031	0.238	2.50	—
Flour (white)	367	12.6	73.1	1.7	0.020	0.092	1.00	—
Fowl	132	24.3	—	3.5	0.011	0.249	2.10	55
Haddock	78	18.1	—	0.4	0.020	0.208	0.50	32
Lemon	19	0.5	3.1	0.5	0.036	0.022	0.60	32
Liver (ox)	129	19.9	4.4	3.2	0.012	0.220	6.70	—
Milk (whole)	66	3.4	4.8	3.5	0.120	0.099	0.12	—
Milk (condensed sweetened)	353	9.3	52.8	10.6	0.330	0.273	0.34	—
Oatmeal	416	11.9	70.0	8.6	0.069	0.392	4.15	—
Potato (new)	90	1.6	20.4	trace	0.013	0.057	0.60	5
Salmon	201	18.4	—	13.5	0.020	0.211	1.03	33
Tomato	22	0.7	4.5	0.1	0.011	0.026	0.37	—
Turnip (new)	24	1.2	4.4	0.1	0.064	0.046	0.33	13

* From Imperial Bureau of Animal Nutrition, Rowett Institute, Aberdeen, Scotland, *Technical Communication No. 10*, 1938; H. C. Sherman, *Chemistry of Food and Nutrition*, The Macmillan Co., Fifth Edition, New York, 1937, by permission of The Macmillan Company, publishers.

one year may cause acute distress because of the difficulty of effecting a carry-over such as is common with wheat, for example.

Like most vegetables, potatoes contain much waste and water and too little inorganic salts, the latter being represented in analysis by the ash. Modern ideas of nutrition stress the importance of these salts far more than previously. Formerly, too, much stress was laid on the fuel (calorific) value of foods, and the inorganic salts cannot be included in this value at all. In the potato the germ is concentrated in the "eyes," and the inorganic salts are found in the large *endosperm* just under the skin. Heavy paring of the potato prior to cooking thus removes much of the inorganic salt content, which, on the other hand, is retained by baking with the skins on—obviously the best method of cooking this valuable food. The protein of the potato is of high grade, and its vitamin content, especially C, is not to be ignored.

Though not of the same botanical family as the white potato, the sweet potato is cultivated largely in regions close to the Torrid Zone. Though less sturdy a vegetable, it is of considerable importance and might with advantage be produced in larger quantities than at present.

420 Beans and Peas

These, either fresh or dried, are important sources of protein, though of second rate, and of inorganic salts and, in the case of the soybean, of fat also. Indeed the soybean is being cultivated more assiduously than ever on this continent, though formerly its habitat was chiefly certain Asiatic countries. Like the other leguminous vegetables, it can fix atmospheric nitrogen; and it is likewise held to be a valuable source of the vitamins A, B and even of C. In addition to its food value, the soybean has come into great prominence industrially. It is used in the making of bread and cakes, coffee substitutes, enamels, soaps and even rubber substitutes. A notable feature of its cultivation is that it will grow in very dry soil.

421 The Tomato

The tomato is more fruit than vegetable, and in the quantity of its cultivation closely approaches the North American potato. It has a very high water content and is low in protein and calories. Since 1925 the juice, pasteurized and canned, has come into general use because of its inorganic salts and vitamin C content.

422 Cabbage and Turnip

These are hardy vegetables. The cabbage is grown largely for eating, either raw or cooked. Of late years its high vitamin C content has raised cabbage to general favor; it was too long regarded as a lowly article of diet.

Turnip juice compares favorably in vitamin value with any other fruit juices now available. If the soil is deficient in boron, turnips tend to be "woody" and hence less useful for food.

423 Fruits

Most fruits, when ripe, consist chiefly of water, sugar, acid and a characteristic flavor. Their fuel value, except in the case of, say, bananas, is usually very low, but their chief value lies in their vitamin C and salt content. In this respect the citrous fruits, such as oranges and lemons, are predominant.

In addition to their food value, vegetables, and fruits particularly, must be regarded as making a definite appeal to the palate because of their taste. This factor is not to be overlooked, for it is much easier to persuade a person to take the necessary amount of a pleasant food than even a very small amount of a richer but less pleasant one. Given a large variety of food materials, the normally healthy people who possess good appetites may well be left to follow their own dietary inclinations; the others—and there are many of them—generally need persuasion.

424 Summary

The fuel value of a food is not the only criterion of food value; fuel value takes no account of maintenance and operation, merely of energy which may be produced. Food value is based on fuel value but is obtained by careful observation of the human metabolism; it is therefore more accurate.

Operation and maintenance involve inorganic salts and vitamins, whose presence is essential to assimilation and subsequent energy production. Thus the foodstuffs must be examined for vitamins, inorganic salts, essential proteins and, last, energy providers.

Protective foods are those which contain the vitamin, calcium and phosphorus supplies in the most digestible and assimilable form—mainly animal products, such as milk and milk products and eggs. Fruits, vegetables and meat supply the remainder of the food materials.

Milk is the most important of all foods. It may appear in its natural form or processed as cream, butter, cheese, etc.—all highly valuable forms of milk because they are concentrated.

The pasteurization of milk tends to destroy the pathogenic bacteria which

may be found in milk without deterioration of the essential food components present. The aging of cheese improves its digestibility.

Milk and its associated products are deficient in vitamins C and D and in iron.

Eggs, particularly the yolks, though lacking in carbohydrate, are rich in fat, proteins (especially the essential ones), inorganic salts and the fat-soluble vitamins.

The grains, barley, corn, oats, etc., are richest in carbohydrate. Their content of inorganic salts, proteins and water-soluble vitamins is largely influenced by the type of processing to which they are subjected for cooking purposes. Wheat is especially rich in gluten, which acts as a binding agent in making bread, cakes, etc.

Meats are richest in protein, fat (variable) and inorganic salts, especially iron.

Vegetables are particularly important for their inorganic salts and vitamin content (notably C). Fruits come in this category also, their fat and protein content being relatively negligible by comparison with milk, eggs and meat.

Modern methods of food preservation include smoking, salting, canning, desiccating and rapid, low temperature freezing.

Questions

1. Are food value and fuel value the same? Why do you think so?
2. What are protective foods? Would you stress foods of animal or of vegetable origin in a protective diet?
3. Discuss the value of milk and its products in relation to food value.
4. What is meant by pasteurization?
5. Compare the grains as to their food values.
6. Stress the relative importance as foods of meats, fish, vegetables and fruits.
7. What action has heat on the vitamins?

30

Diet

425 The Human Machine

The preceding chapters on foods have designedly represented the human body as a machine which needs to be fed with certain raw materials before it can prepare the products necessary to the maintenance of its efficiency and to the repair of its various parts. This may be a beautifully adjusted machine and automatic in its functioning. But here the analogy ends, for many factors enter in now and tend to set the human body apart not merely from inanimate machines but also from the bodies of other animals.

Man develops slowly from an embryo, whose prenatal life depends upon the adequacy of its food supply and possibly inherited tendencies. At birth he is extremely helpless and, though complete as to organs, is required to spend a score of years before his body has attained that maturity which permits him to function as a perfect machine. Dietary deficiencies during this period of development (and even before) determine very largely how efficient this machine can be at maturity. Within the next score of years, his mechanical efficiency is presumably at its best; but, at the end of this period, the machine begins to show those signs of change which require a material lessening of mechanical activity. This change is nowhere better exemplified than in the development of the bony tissues. That normal mental development reaches a maximum at a later date is definitely to the advantage of the human species, which can "take thought for the morrow." But this mental growth is not by any means independent of external influences, particularly in a civilization which makes such mental and physical demands upon the constitution as our present one.

Important factors, therefore, appear which have no counterpart in the mechanical analogue. They are the changing conditions of

material growth and decay, the vastly different kinds of work done in different walks of life, the different climates inhabited, seasonal changes, the different foods characteristic both of climates and of seasons and lastly the various psychological factors which tend to influence the various human mechanisms. Mental resourcefulness has permitted man to adjust himself to great climatic and seasonal changes well within his lifetime—so different from the migratory birds, for example. The considerations applicable to a machine, as well as a modicum of common sense, will serve to enable man to keep himself mechanically in as nearly a perfect state of activity as is characteristic of his age. But when the machine breaks down because of accident, infection, dietary deficiency, etc., a pathological condition ensues which calls for the skill of the expert physician or surgeon. Although the art of healing has always been recognized as one function of medical science, it is only within the last thirty years that the prevention of disease has come to be recognized as a greater art. Nor has physiology alone received all the attention, for psychological influences increasingly call for consideration by specialists.

426 Hunger and Appetite

In this preventive scheme the diet plays a greater role than is generally realized. The principles already enunciated stress the necessity of the contribution of carbohydrates, fats, proteins, inorganic salts and vitamins to daily sustenance, and to the production of the heat energy required; but it has been stressed that any foodstuff supplying the appropriate number of calories is not necessarily bound to be digested. An excess of any food, such as one high in protein content, over a limited period of time may result in a loss of all over the amount that can be digested. Many foodstuffs become tiresome and unpalatable if taken frequently. *Hunger* is a definite expression by the digestive tract that food is required, and is not to be confused with *appetite,* which is not necessarily satisfied at the same time as hunger. For after a completely satisfying meal one can still eat with enjoyment a sweet confection because of its flavor; and a hungry person may turn away from a poorly prepared dish of high food value.

It should be noted that both hunger and appetite may be temporarily satisfied by foods which are really of little value either as energy sources or for "protection." One considerable advantage

of cooking is that it commends the flavor to the taste, thereby stimulating the digestive secretions, so that the food may be called appetizing. Appetite is largely dependent on childhood habits and early training. The sensations and effects of fatigue and worry are well known causes of even rapid loss of appetite, though hunger may be only too apparently present. In fact very little is required to upset the appetite. All these effects may be regarded as the "personal equation" of the consumer. Vitamin deficiency often causes loss of appetite so that less and less of the vitamin is consumed. Fortunately there are some foodstuffs which are appetizing to all normal people of any particular race or climate; but there is a number of articles of diet for which certain people have a distinct distaste. Frequently this distaste may be the result of unsuitable preparation of the food.

427 The Art of Eating

Provided that all the necessary elements of diet are available, there still remains the fact that eating is an art—a fact of which many seem not to be aware. Starchy foods represent a large proportion of any daily diet, and they require mastication, which includes mixing with the saliva. Besides being a lubricant, saliva contains the amylase ptyalin which initiates carbohydrate hydrolysis in the mouth. More time for the eating of any meal has two definitely beneficial effects, more thorough mastication and the greater enjoyment of the flavor of the food, which has its reward in the stimulation of the digestive tract to take care of the eaten food.

A further factor of importance is the mechanical stimulation of the digestive tract. The very young child finds a satisfactory diet in milk and a fruit juice. But as the age increases so must the size and capability of the stomach and intestines increase. For the mechanical stimulation of the organs a certain amount of roughage is essential. A diet of milk, soluble carbohydrates, liquid fats, etc., is inadequate, so this roughage is supplied by vegetables with their content of indigestible cellulose, crude fiber.

A healthy hunger and appetite, the results of physical exercise, provide the best setting for the ingestion of food. Under such circumstances stimulating spices, for example, are unnecessary; and their use is to be deprecated as they merely overexcite the glands which provide the digestive juices. For jaded appetites, condi-

ments have their place, but even then they should be used sparingly.

428 Dietetics

The dietetic art takes into account all the above factors, in addition to providing for those who, because of some physiological defect, are unable to have a general diet. It requires a knowledge of the dietary components of all ordinary foods and the ability to select those which will provide daily all these components in desirable quantity. Such a daily regimen of carbohydrate, fat, protein, inorganic salts and vitamins is known as a *balanced diet.*

Here, then, is the problem facing the dietitian in formulating a twenty-four-hour menu: enough bulk foods to supply the energy required for a certain age, body weight, sex and habits; all the inorganic salts and vitamins in such quantity as are necessitated by the same conditions; and the amino acids previously mentioned as essential components of proteins. Considerable latitude is permissible in the proportions of carbohydrates and fats since both are essentially energy producers. But if a high caloric intake is required, the food becomes too bulky unless plenty of fat is included. In addition, the apparent likes and dislikes of the eater are to be taken into account, and the twenty-four-hour menu must show considerable variety. When this is outlined for one day, care must be taken to fulfill these dietary requirements for the next day and the day after without undue repetition. Change may be accomplished by different cooking methods, particularly for the protective foods, which act as a foundation on which the menu must be built. When perhaps all this is neatly arranged, one is confronted by a constitutional allergy in the eater, where the presence of some one article of diet proves poisonous, giving rise to all kinds of skin and other afflictions. Nor can this condition be blamed on food—it is rather the hard luck of the eater. Truly the dietitian's task is a hard one, but science has made it much less haphazard than formerly; and such care in nutrition is rewarded in the added health of that nation which takes the food problem seriously.

429 Adulteration

The chief safeguard in the processing of foods relates to adulteration. In this respect conditions once were such that stringent legislation was required to stop obvious abuses. For example, a

product labeled strawberry jam and nothing else should be, of course, nothing else; to substitute turnips, apples and timothy hayseed for strawberries is too imaginative to be honest. But the addition of pectin—to cause the fruit juice to jelly—if so advertised merely provides a product with fewer strawberries (and therefore somewhat cheaper in price) but with a satisfactory food value, since the attraction of the strawberry is its flavor. Similarly margarine has its place in any list of foods, as long as it contains an appropriate amount of the vitamins found in butter. The hydrogenation of cottonseed and other oils to produce edible fats is not merely justifiable but good sense. The truth of the matter is that the word *substitute* is too often confused with the stigma attached to the word *adulteration*, which implies the addition to an honest product of a baser material. Abuse of privilege is as old as man, and the class of commodities that positively should not be tampered with is food.

Modern methods of food preservation trust more to low temperature storage and to high temperature sterilization than to addition of chemical preservatives. In any event, the oft-repeated admonition to eat fresh foods whenever possible is a protection to the adult. Incidentally it should be noted that canning often causes less vitamin loss than ordinary methods of cooking. For children the water and milk supplies are of greatest importance, and difficulties here arise only in straggling communities and not in well-organized towns and cities.

430 Food Preservation

Preservation of food in modern times has changed because of several developments: (1) better methods of bottling, whether commercial or domestic, (2) improved canning with the elimination of lead or solder sealing and (3) refrigeration. Meats could formerly be kept only in cold rooms, not unlike the underground cellars still found on farms, and they offered no guarantee that the food would stay fresh except in winter. As an alternative the meats and fish were variously processed by salting in a mixture of salt and saltpeter or by smoking and salting or by a combination of smoking, spicing and salting. Pork products such as hams and bacon are still treated so, and the same is true to a small degree for certain fish, but the similar treatment of beef and mutton has become almost a lost art. Such methods require long treatment, and

where the treatments are hurried a uniform product is not maintained. A definite advantage to this processing is that it tends to soften the hard fibers so noticeable in freshly killed beef or mutton. To some extent this is effected by allowing carcasses to hang for several days at a temperature just above the freezing point. Slow freezing very definitely destroys the texture of meat and fish and may render fish quite flavorless. Modern methods of canning of both kinds of food has made export to hot climates a successful reality.

Of recent years rapid, low-temperature freezing has revolutionized the keeping of fish, vegetables and fruits. These foods are frozen immediately and must be kept in refrigerators until purchased. Unless kept cold in the domestic refrigerator they must be used as soon as they have been thawed out. If these precautions are followed, such products as peas, beans, berries and fish appear to have their original texture and flavor and, of course, contain no waste. Since the ordinary ice refrigerator is always above 0°C, the storage of such frozen foods requires electricity. Liquid nitrogen at −191°C has been used for freezing food, though liquid ammonia (−70°C), with tanks of calcium or sodium chloride, is more common.

Fruits picked for canning or refrigeration must of course be washed, particularly if sprays, frequently containing arsenic compounds, have been used to destroy insects while the fruits were still on the trees. Fruits are frequently picked green and ripened in transit if the market is distant from the source of supply. A ripening agent which has attained considerable popularity is the gas ethylene which is not known to produce any harmful results in this instance, though it may be used in quantity as an anesthetic. The fruit so ripened is therefore really fresh, although it may have been picked a considerable time previously.

Such preservatives as sulfur dioxide and sodium benzoate have been used to preserve bottled fruits, but their use has to a great extent been curtailed by public disfavor. Such preservatives for vegetables as are permitted by health authorities need cause no worry, but no chemical preservative for meat and fish can be tolerated. Other than refrigeration there is only salting, smoking, spicing or a combination of these, which actually may make meats more digestible than the fresh product. Note the widespread popularity of smoked bacon. Milk, of course, should never be

treated with a preservative, although it is very susceptible to spoiling if not pasteurized. Hard vegetables, such as turnips and carrots, may have their moisture and flavor retained by a coating of paraffin, which is easily removed prior to cooking, and could do little harm under any circumstances.

After pasteurization (148°F) or boiling (or 212°F at most) fruits may be preserved in sugar, which is then not merely a sweetening agent. Fruits so preserved may be in the liquid or semi-solid state, as jams. The container for liquids must be tight to keep the liquid in and bacteria out. If the jam contains sufficient sugar such precautions are not so necessary. Condensed milk with its high sugar content keeps indefinitely while unopened in all kinds of climatic conditions and even when open to the atmosphere retains its full value for a long period of time. It is the most important preserved food known.

Desiccated foods arose out of the demands of export. When properly dried and later allowed to absorb water they represent something very close to the fresh product. Their great advantage is in cost of handling and transportation since even meat and fish contain 70 per cent water. Since grains today constitute the bulk of foodstuffs for the people of the world, it is fortunate that nature has provided that they both ripen and are desiccated before harvesting. As long as they remain dry in the coarse or milled state they require no special kinds of preservation. In the household, however, in the conditions prevailing in the kitchen, oatmeal and ground corn do not keep indefinitely; their high fat content is conducive to souring. Oatmeal is an excellent breeding ground for moths, for example.

It has long been found necessary to remove some of the germ from wheat in order to prevent deterioration. This wheat germ is rich in B and E vitamins, particularly in B, and is an excellent source of vitamin reinforcement of the diet. The wheat germ oil, also, has value as a food preservative.

Our new knowledge of foods, gained largely by the demands of war, has had results in other than the human fields. Perhaps nowhere is this more apparent than in the improved methods of poultry raising, which assume considerable importance because of our shrinking areas of farm and grazing lands. The time will come when, with increasing population and lengthened life, we shall be unable to have both bread and beef. Soil erosion, though un-

doubtedly aided by man with his mining methods applied to farming, is nevertheless a natural phenomenon—the Mississippi is evidence of this.

431 Summary

A proper diet is essential even before birth to insure the presence of all the elements which make for growth. When full physical growth is attained the same general considerations hold, though with regard to maintenance rather than growth.

At all ages a protective diet is necessary, as much as a preventive of disease as a corrective. On this protective diet can be built the quantities demanded for energy and maintenance of the human machine.

Even when all the elements of a good diet are present, the individual response to appetite, hunger, or both, must be of a nature that will utilize the food offered. Fatigue, nervous irritability, cooking, etc., are all factors that influence the digestion and assimilation of food.

For the young child easily assimilable foods are essential; for the adult a certain amount—though not an excess—of roughage aids digestion by stimulating the alimentary tract.

Dietetics is the art of arranging balanced diets, that is, twenty-four-hour schedules of meals that will contain the protective foods (with their protein, inorganic salts and vitamin content) together with the energy-giving carbohydrates and fats demanded by the age and type of work of the consumer.

Food is the first commodity of a nation to be safeguarded. Adulteration is the substitution of inferior materials for superior ones—a practice to be deprecated. But wise substitution under qualified control may frequently be advantageous.

Modern methods of food preservation rely on low-temperature storage, desiccation, and canning. These are extraordinarily efficient and obviate the use of preservatives which can be harmful.

Questions

1. Are hunger and appetite the same?
2. What factors other than a well-balanced meal may enter into the digestion of food?
3. What do you understand by the term dietetics?
4. Is substitution the same as adulteration?
5. What general methods are adopted in the preservation of foods?

Part 4

INDUSTRIAL CHEMISTRY

31

Raw Materials and Their Sources

432 General Sources of Supply

Chemistry is at the mercy of sources of supply for the materials needed to carry on industrial manufacture and experimentation. In the preceding pages reference has been made to the various countries and districts from which special materials are procured. Irrespective of these particular areas, general sources of supply may be classified as follows:

$$\left.\begin{array}{l}\text{The Atmosphere}\\ \text{The Hydrosphere}\\ \text{The Lithosphere}\end{array}\right\}\ \text{The Biosphere}$$

The atmosphere contributes its nitrogen, oxygen and rare gases; the hydrosphere is the chief source of water and hydrogen, in addition to supplying in certain localities such dissolved solids as common salt; the lithosphere supplies all the metals, most of the non-metals and the accumulation of coal, petroleum and natural gas. In addition we have the biosphere (or life realm), whose products grow out of the lithosphere into the atmosphere and hydrosphere—the vegetable kingdom—and the animal products whether on land or in the sea.

433 Tapping the Reservoirs

The methods employed to obtain available supplies depend largely upon the type of source; the gases of the atmosphere and the water and aqueous solutions of the hydrosphere are pumped into the apparatus designed for their treatment.

The contents of the lithosphere are extracted mainly by processes which are included under the name of mining. This applies to deposits of aluminum, sulfur, sodium, potassium, phosphorus, iron,

manganese, etc.—all inorganic in nature—as well as to the stored deposits of biogenic origin, such as calcium carbonate, coal, petroleum and natural gas.

Products of the biosphere may vary from wheat, cotton, wood, on the one hand, to fats on the other.

The previous sections of this book have provided a more or less detailed survey of the chemical elements and their compounds with scant reference to the sources from which they have come and the means by which they have been prepared for chemical investigation and treatment. The remainder of this chapter is devoted to a study of the lithosphere as a source of chemical raw materials.

434 The Lithosphere

The study of the lithosphere and its relation to the atmosphere and hydrosphere lies within the scope of the geological sciences; the sources of raw material are the special concern of one branch of these sciences, economic geology.

The average composition of the lithosphere to a depth of ten miles has been determined by many hundreds of analyses (see Table 20, § 227). One fact that stands out after inspection of this table is that some of the best-known elements occur in proportions so minute that their extraction from the average rock is not feasible; in other words the average rock does not constitute an ore of any metal. It is only where the desirable material has been segregated that it may be extracted at a profit. This segregation is brought about principally by chemical processes and, to a minor extent, mechanically.

435 Formation of Deposits

Every process known to the chemist has its natural analogue and has, in most instances, played a role in the formation of some ore deposit. Thus distillation, fractional crystallization, precipitation, sublimation, solution have all contributed to such deposition. Sometimes the processes acted within a silicate melt; at other times the medium was water at a normal or elevated temperature. In fact, in explaining the origin of many ore deposits the geologist has been engaged in reconstructing a chemical reaction from its fossil products. This reconstruction frequently leads to the conclusion that a very large class of ore deposits was formed from dilute aqueous solutions at a temperature between 100°C and

600°C; this in time deposited the ore (valuable) and the gangue (useless or less desirable minerals). These deposits form lenticular masses known as *veins*, which are usually long with respect to their thickness and are commonly nearly vertical. In some places favorable zones for mineralization have other attitudes. Deposits of the type which are caused by solutions coming from a depth are known as *primary*.

In secondary deposits the agents of weathering have concentrated the elements contained either within the lithosphere or from veins in it. Such deposits are of course formed near the surface, and many very rich bodies of this type have been found. The placer gold deposits are historically interesting members of this group, and many metals such as platinum and tin have to some extent been won from placer deposits. The placers, or detrital deposits, are only one category of *secondary* deposits.

Material may be carried in solution by water to a lake or the ocean and there deposited. For example, some of the iron ores are from bogs, whereas salts such as the chlorides of sodium and potassium were precipitated from the ocean. Although secondary deposits are formed near the surface, many were buried by younger rocks and must be mined in the same way as vein deposits or coal.

436 Ores

The term *ore* was formerly restricted to the mineral or minerals from which the more valuable metals were extracted; but this term has now been extended to include non-metallic substances for which the deposits are exploited. The useless minerals are the gangue. Some gangue minerals, however, are sold or utilized, though their value is such that the deposit would not be exploited for them alone.

437 Classification of Ores

Ores may be classified under two heads—the metallic and the non-metallic. This distinction is obvious. The first class is used as a source of metal only; the second class is important for some property inherent in the material itself, for example, asbestos for its insulating value, or barium carbonate as a source of barium salts for chemical use. Recently a new term has come into prominence—*industrial minerals*. An industrial mineral is used in general for its physical or chemical properties, or as a source of metal

or product obtained by chemical rather than strictly metallurgical processes. This distinction is not hard and fast, and a mineral may fall into more than one category, depending on the use made of it.

Most of the ore minerals are compounds of the metals with sulfur, oxygen or carbon dioxide—the sulfides, oxides, carbonates. Only occasionally are silicates useful as a source of metal. and many of the non-metallic ores are silicates.

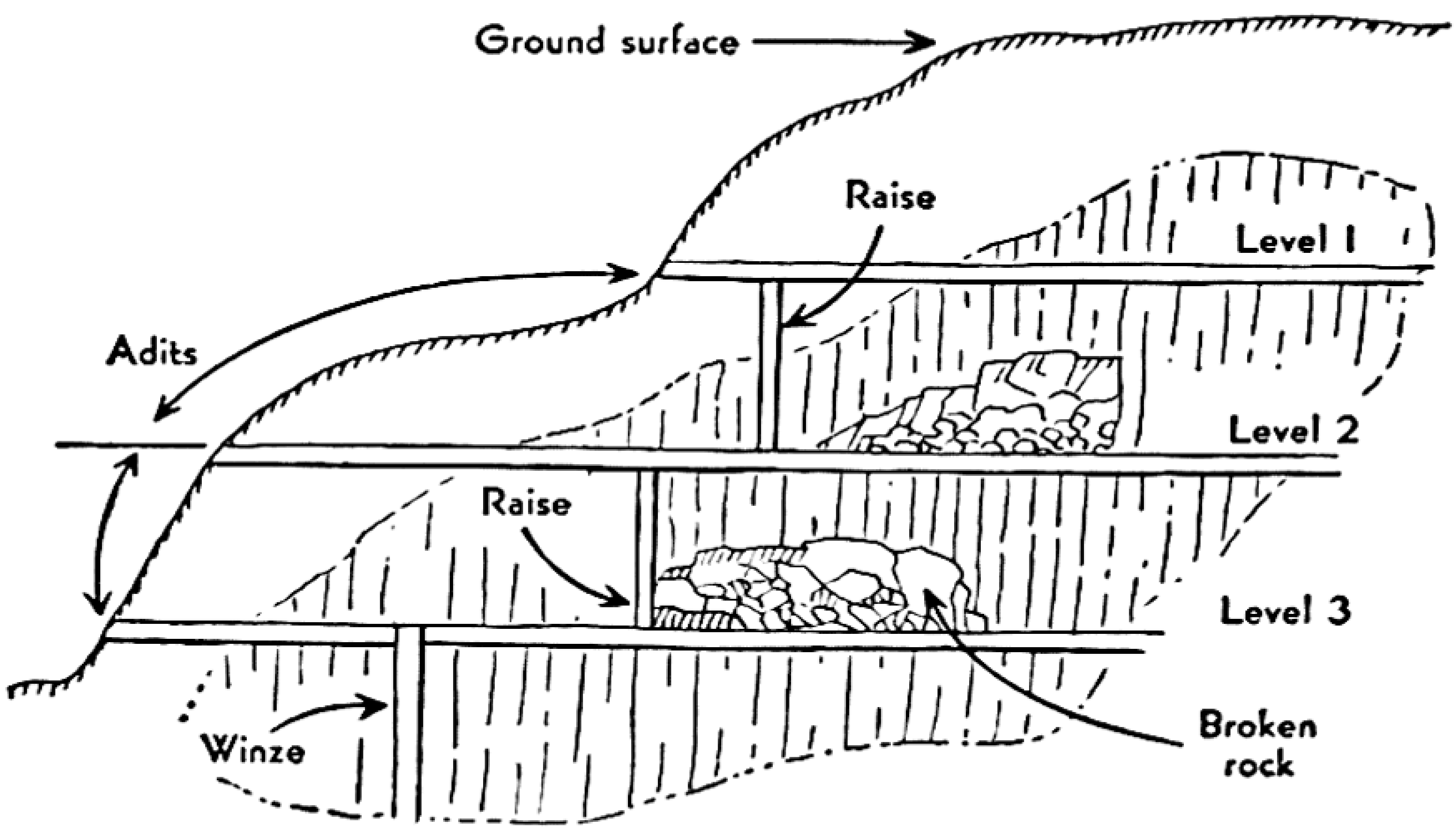


FIG. 72. Vertical section outline of ore shoot on a steep vein.

438 Mining

It is obvious that mineral raw material is useful only after it has been removed from the ground, and it is the work of the mining engineer to accomplish this removal as cheaply as possible.

In some places the material is open to the surface and may be taken out from open pits or quarries. These surface openings, however, cannot be used to remove material more than a few tens of feet below the surface; and for deeper deposits mining technique must be employed.

A series of more or less horizontal levels is opened in the deposit to serve as haulage ways (Fig. 72) and means of access. Work is commonly started above the level and a working place or stope formed. The broken material falls through chutes into cars to be trammed to the surface or to a shaft (Fig. 73). The levels are usually about 150 feet apart, and the work on them alone is part of the development.

Variations of the simple scheme here outlined are necessary if the surrounding ground needs much support or if the ore body is not sufficiently steeply inclined. A different set of terms is employed in coal mining, and the methods are slightly but not fundamentally different.

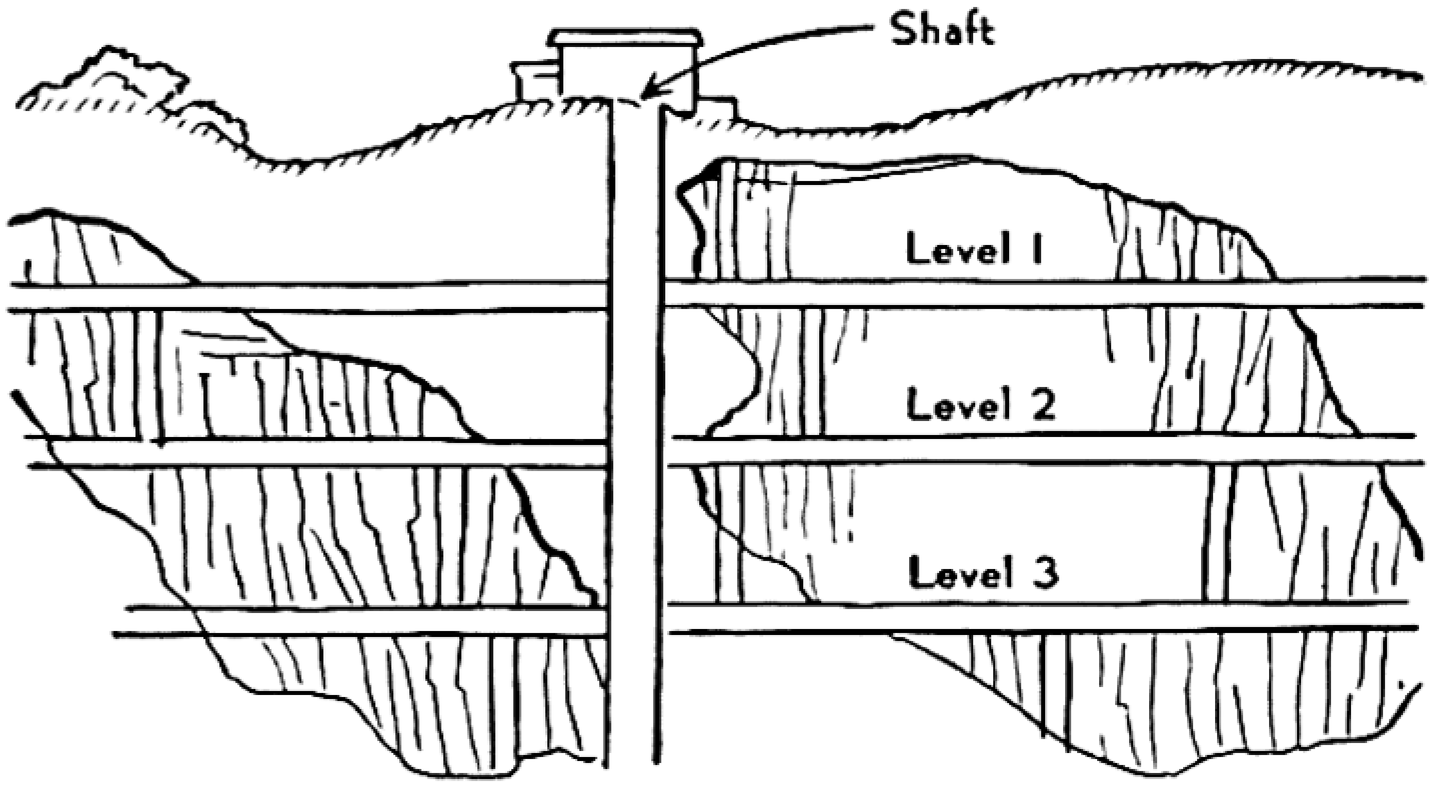


FIG. 73. Vertical section of a shaft mine.

439 Beneficiation

The ore so won may contain a large amount of waste or gangue, which must be removed before the material can be marketed to the consumer or sent to the smelter. The diversity of physical properties of the two are used to effect the required separation. Most ore minerals are denser than gangue so that the finely crushed material may be divided into fractions by gravity. This separation is normally effected in water, and the machines used are jigs or shaking tables; the ore forms the *heads* and the gangue the *tailings*. The material may be fractionated by magnetic or electrostatic machines; but the most important method is *oil flotation*. This method depends on the fact that air bubbles in water with suitable reagents become attached to the minerals of metallic luster and float them to the surface, where they can be skimmed off; whereas the gangue remains at the bottom of the container. By conditioning with suitable reagents (organic and inorganic) some of the metallic minerals may be floated in preference to others, and it is thus possible to separate sulfides of copper, lead, zinc and iron.

The beneficiation of gold calls for special comment. This metal occurs in small amount, an ore with one Troy ounce of gold in a ton of rock (29,166.7 ounces) being very rich; yet it is not unusual for 96 per cent of the gold in an ore to be recovered. Gold is in

part recovered by gravity and flotation methods, but *cyanidation* and, to a lesser extent, *amalgamation* are also employed.

Cyanidation is simply a process of solution whereby finely ground gold ore is agitated with a weak solution of sodium or potassium cyanide. The solution containing the gold is then passed through charcoal or zinc which precipitates the metal. Amalgamation is possible because gold combines with mercury to form an amalgam. The ore is passed over mercury on copper or is agitated in a barrel and the gold is trapped; it is recovered by boiling off the mercury.

The beneficiation and processing of the non-metals are largely dependent on the specifications of the consumer. A discussion of these factors is beyond the scope of this book.

440 Coal

Coal is mined in much the same manner as an ore; it is then screened, washed and shipped wherever required. The type used in the production of coal gas and coke is bituminous, which runs from 50 to 75 per cent carbon.

441 Sulfur

Sulfur occurs free in the vicinity of active volcanoes and is found impregnating the rocks. It may be freed from them by piling the rocks in heaps and igniting them at the bottom; the burning sulfur produces enough heat to melt the upper layers. The molten sulfur may then be run into molds, where it solidifies. This is the procedure adopted in Sicily, which until the turn of the century was the chief source of sulfur.

In Louisiana and Texas are large deposits of relatively pure sulfur well over 400 feet underground, and here the Sicilian method is quite unsuitable. From this depth it is obtained by the Frasch method, an ingenious scheme for melting the sulfur underground and then pumping it up. Briefly, this is accomplished by means of concentric pipes reaching down into the sulfur bed through a hole previously drilled through the overlying rock and earth. Through a large outer pipe superheated water is pumped under pressure on to the sulfur, which is thereby melted. This water is followed by hot air under high pressure, whereupon a mixture of air, water and molten sulfur is forced up to the surface. This material is pumped into large wooden tanks, where it solidifies. The sulfur so produced is very pure, and for general purposes needs no refining.

442 Petroleum

This is obtained by drilling through intervening layers of rock, a mixture of petroleum and water usually being forced out under pressure. Petroleum found on this continent is generally accompanied by large quantities of natural gas, mainly methane. Where a gusher so-called results from boring operations it is necessary to cap the hole in order to control the supply. This crude petroleum requires distillation in order to separate it into the various industrially useful fractions (§ 514).

443 Common Salt

Sodium chloride is frequently found in large subterranean deposits on this continent. But on the west coast of Africa it is obtained from sea water by evaporation. The principal use of this local product is in providing a form of currency for the natives of the interior; for this purpose very fine crystals of the salt are compressed into blocks about $\frac{1}{2}$ by 1 by 2 inches. It also serves as a condiment for the natives of the interior who possess no salt deposits.

444 Summary

Chemical raw materials come from four sources, the atmosphere, the hydrosphere, the lithosphere and the biosphere. The atmosphere supplies oxygen, nitrogen and the rare gases. The hydrosphere supplies water and certain dissolved salts, such as common salt, magnesium sulfate. The biosphere represents living matter, as plants, land animals and fish. They provide a large variety of products, such as carbohydrates, fats, wool.

From the lithosphere come all the metals and most of the non-metals, including such biogenic products of the past as coal and petroleum.

The science of mining is the extraction of raw materials from deposits in the lithosphere. These deposits have accumulated as the result of such processes as solution, distillation and precipitation, well known to the chemist but on a vaster scale, of course.

Veins are ore deposits concentrated in relatively narrow threads; they are primary deposits coming up from a depth in the ground. Secondary deposits result from weathering and occur near the surface, for example, placer gold deposits.

Ores are the more valuable mineral deposits; the useless materials associated with them are called gangue. Ores are classified as metallic and non-metallic, for example, iron oxide and sulfur. In addition, other minerals are mined, not for their metal or non-metal content but for their industrial importance, asbestos, for instance.

Mines are excavations in the ground to remove the ores contained therein.

Beneficiation is the term applied to the separation of the ore from the

gangue. This may be effected by gravitational, electrical or flotation methods. Gold may be separated by solution in sodium cyanide or mercury—cyanidation and amalgamation.

Sulfur is mined by melting underground and blowing to the surface (the Frasch process). Petroleum is obtained by drilling through the intervening rock and entrapping the effluents.

Questions

1. Name and explain the four spheres of supply of chemical raw materials.
2. What in general are the chief products of each of these spheres?
3. What do you understand by the terms ore and gangue? What is a vein?
4. What are the main principles adopted in mining? What is beneficiation?
5. How may ores be classified?

32

Industrial Chemistry, Metallurgical Processes

445 Chemistry, Pure and Applied

A distinction may be drawn between the study of the elements and their compounds for the sake of present and future knowledge of their behavior and the large-scale production of these same substances to supply the needs, not merely of the chemical investigator, but also of the world at large. This distinction is really not a sharp one and is rather a matter of the quantities involved. True, the industrial application of a chemical process has to be worked out in the laboratory first before it can be applied on a large scale. But the large industries conduct researches in pure chemistry just as do their academic counterparts; both employ the same theoretical principles, the same raw materials, the same technique. But chemical industry needs the services of the trained engineer, whose design of apparatus, for example, must take into account the stresses caused by high pressures, etc., on large units, whereas such factors are of less importance in the laboratory.

Let us suppose that a new substance has been discovered which would appear to supply a present or future demand, perhaps in competition with one already generally accepted by the public. It is in what we call the test tube stage, and perhaps a considerable amount of money and of time has already been spent upon it. To develop, this discovery must pass into the pilot plant stage, where large quantities of raw materials and specially designed apparatus are employed to discover and control the various factors which will make for successful large-scale operation. This kind of study may well involve changes from the original experiments until at last the final product appears ready for presentation to the buying

public. It may well be that up to this point many millions of dollars have been spent without even the possibility of any returns for the investment. The worries of the company management now include financing the project, costs of raw materials and their transportation to the plant, costs of power (such as electricity or coal), of packaging, of transportation to buying centers, of insurance, of maintenance, of manpower and a myriad other costs incidental to the marketing of the product. If the product is successfully marketed, the whole cost of research and plant should be paid for within about five years, for if it is not then it is not impossible that a newer discovery will place a newer and better article before the public. Thus it takes some time for the selling price of a new article to drop down to within that of some previous commodity now partially or completely replaced. If, however, the new article does not sell, the loss has to be borne by the company concerned.

A little thought at this point will indicate the far-reaching effects of cotton growing in Egypt, of the synthesis of nitric acid from the atmosphere, of synthetic fibers, of plastics and many other similar examples of modern industrialization.

446 Metallurgy

This and the succeeding chapters will present selected types of chemical processes whose importance is worldwide because of the quantities of chemical products to which they give rise. The ramifications of chemistry are such that it is becoming increasingly difficult to draw the line between chemical and non-chemical industries. Consequently, included in the following pages is a brief outline of the science of metallurgy, which though considered separately from chemistry nevertheless employs chemical reactions and chemical principles. Indeed, as has been pointed out previously, the beginnings of chemistry were metallurgical, and so it is fitting to include a brief treatment of the science to which inorganic chemistry owes so much.

Metallurgy is the art and science concerned with the recovery of common metals from their ores; it also embraces the study of the behavior of metals and their alloys under diverse conditions. Though formerly devoted to this recovery by heat treatment principally, metallurgy now utilizes electricity to an increasing extent.

The processes of metallurgy are largely chemical reactions at a high temperature, and the metallurgist is guided by principles identical with those normally associated with theoretical chemistry. Here we shall consider chiefly the classical aspect of metallurgy—pyrometallurgy.

447 Pyrometallurgy

Roasting. After the ore has been milled and concentrated (§ 439) the chemical processes are applied which remove the metal from the compound. One of the common types of ore is a metallic sulfide. Before the smelting process takes place, the sulfide is converted into an oxide by a process of roasting, that is, the ore is heated in ovens or furnaces in a current of hot air. The oxygen unites with the sulfur to form sulfur dioxide which passes off as a gas, and oxygen also unites with the metal to form the metallic oxide

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \uparrow \quad (147)$$

If the ore is in the form of a carbonate, heating alone is all that is necessary to convert it into an oxide.

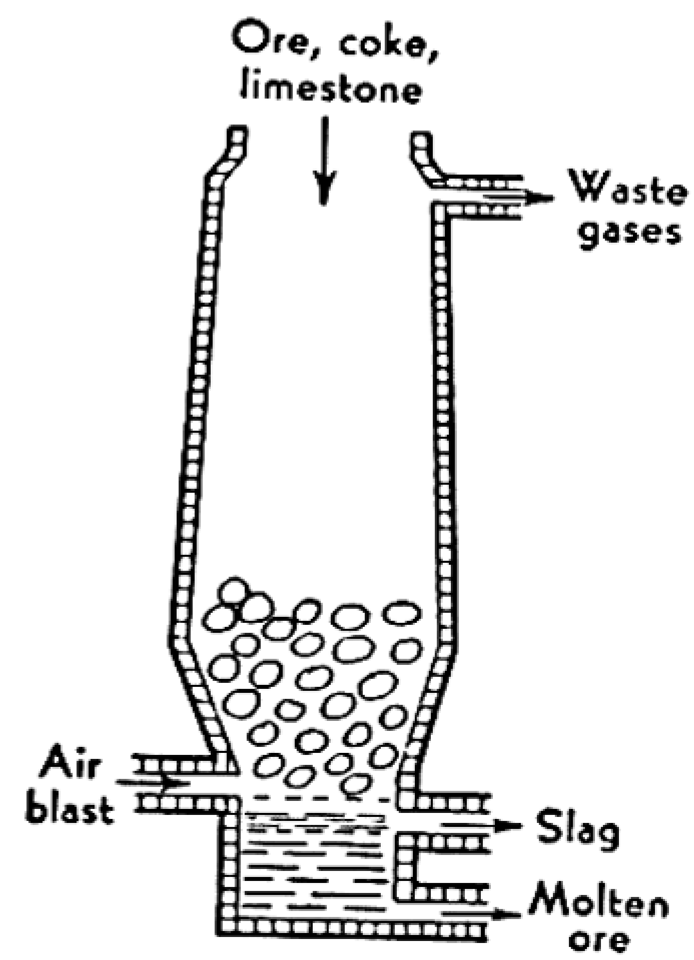


FIG. 74. A blast furnace.

Reduction. The sulfur has now been removed, and only the oxide and the gangue remain to be eliminated in order to obtain the metal. In recovering metals from their oxides by heat treatment, two general types of furnace are in use.

In one, the blast furnace (Fig. 74), the crushed ore is mixed with the fuel (coke) and air is blown in at the bottom. The ore is thus reduced to the metal by carbon or carbon monoxide. The molten metal and the slag trickle to the bottom of the furnace and are removed through separate openings. In the other type of furnace, the reverberatory, the material to be reduced (or melted) does not come in direct contact with the fuel, but is heated by a radiant flame such as that given off from powdered coal.

Slag is a by-product of all smelting operations. It is a solution of easily fusible silicates formed from the gangue components of the ore and from the substances (flux) which are added in order to give the slag a low melting point or increased fluidity. In practice

the slag consists of silica, lime, magnesia, alumina and oxides of iron. Such a slag does not dissolve molten sulfides or metals, and, being lighter than either, it forms a layer over them just as oil overlies water. The slag may then be tapped by holes in the furnaces below the slag line but above the top of the metal, the metal or molten sulfides being removed at a lower opening.

448 The Smelting of Iron

The principal place of the blast furnace is in the reduction of iron. Such furnaces may be more than 100 feet high. The ore is fed with coke and flux at the top and is reduced by the hot gases and the contact with carbon during its travel down the furnace, so that molten slag and metal are tapped at the furnace bottom. The product of the blast furnace, high in carbon and silicon, is known as pig iron. In some processes the molten pig is poured into large caldrons known as Bessemer converters (Fig. 75), through which a blast of air is passed. The air oxidizes part of the carbon and silicon. At the same time any necessary alloying substances such as manganese, titanium, molybdenum and tungsten are added. The product is steel. In another process the molten pig iron, cold pig iron or scrap iron is put into a type of reverberatory furnace known as an open hearth (Fig. 76). Ore containing oxygen is added to oxidize the excess carbon of the

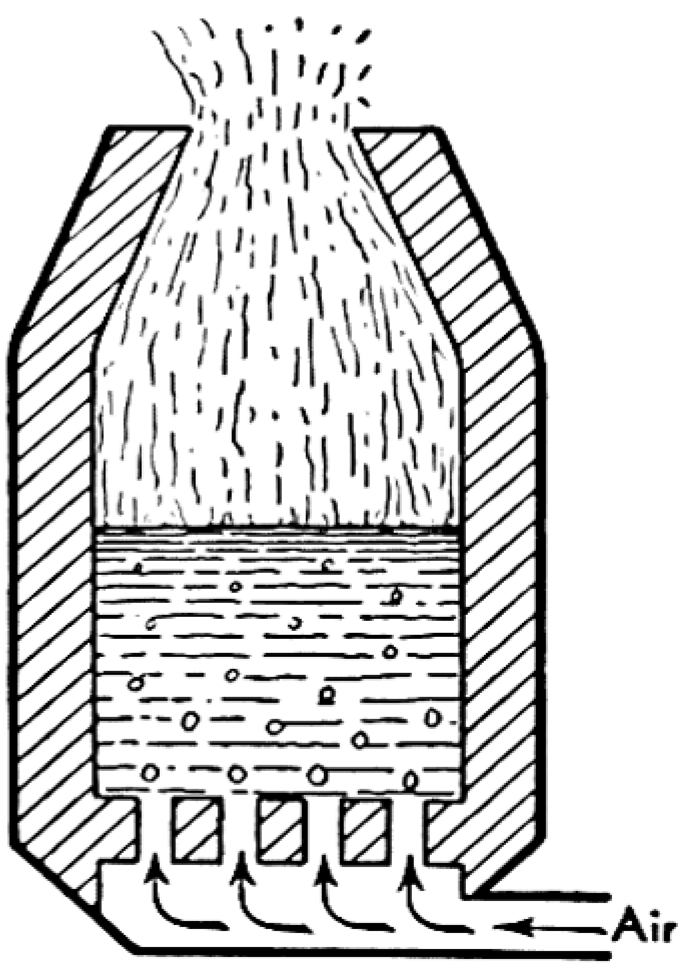


FIG. 75. A Bessemer converter.

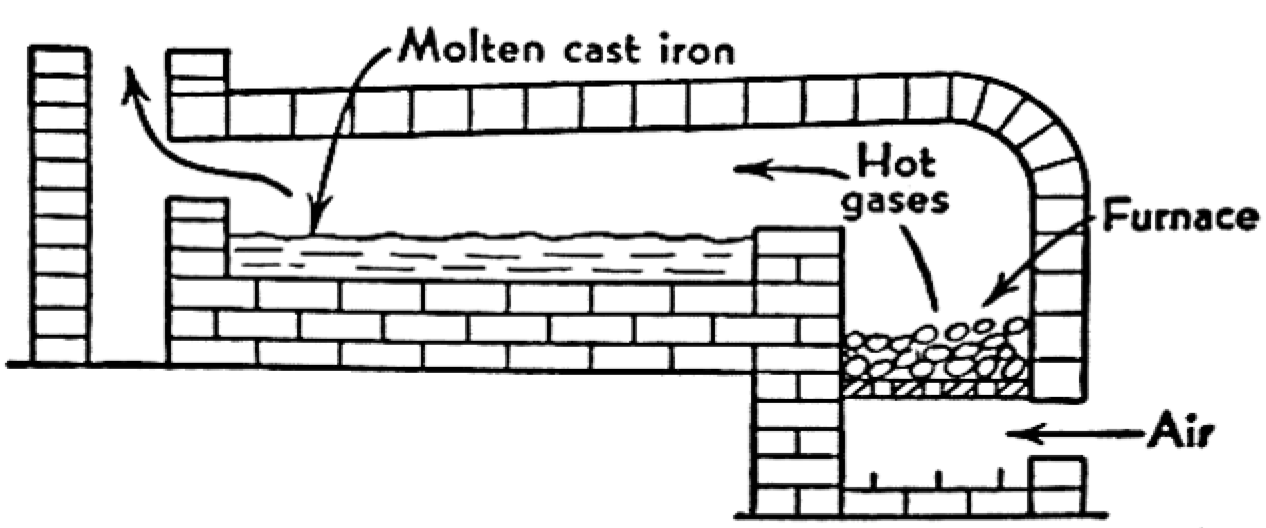


FIG. 76. An open-hearth furnace.

pig iron, and the alloy metals are added. Depending on the kind of linings they contain, the open hearths are acid (silica lined) or basic (magnesia or magnesia-lime lined). The choice of lining

has a bearing on the final properties of the steel and on the impurities which must be eliminated.

The iron ores used in this reduction are the oxides hematite, limonite and magnetite and the carbonate siderite. This reduction, though somewhat complicated in practice, may be represented by these equations:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \tag{148}$$

Decomposition of the limestone flux

$$CaO + SiO_2 \rightarrow CaSiO_3 \downarrow \tag{149}$$

Union of lime with silica to produce the molten slag

$$C + O_2 \rightarrow CO_2 \uparrow \tag{150}$$

Coke burning vigorously to produce carbon dioxide

$$CO_2 + C \rightarrow 2CO \uparrow \tag{151}$$

Carbon dioxide reacting with hot coke to produce carbon monoxide

$$3CO + Fe_2O_3 \rightarrow 2Fe \downarrow + 3CO_2 \uparrow \tag{152}$$

Carbon monoxide reacting with iron oxide to given molten iron and carbon dioxide

The cooled iron obtained as in equation 152 is pig iron.

449 Cast Iron

Pig iron as it comes from the blast furnace is too brittle for most uses as a result of the impurities. These impurities also cause the pig iron to have a lower melting point. Pure iron melts at about 1530°C, while pig iron melts at 1100°C. In making cast iron the pig iron is heated in a cupola furnace with coke. Some of the impurities are burned out, and scrap iron is usually added. The molten iron is then poured into sand molds. Stoves, radiators, machine bases and other articles which are not subjected to sudden stress are made in this way. Cast iron is hard and brittle. It cannot be rolled or forged. Its chief advantage is its cheapness.

450 Wrought Iron

This is the purest form of commercial iron. It is being replaced to a large extent by low carbon or mild steels. It is made by heating pig iron on a bed of iron ore in a reverberatory furnace. The flames are deflected from the roof of the furnace and the pig iron is melted. The oxygen from the iron ore oxidizes the carbon and other impurities in the pig iron. As the impurities are removed, and the iron becomes more nearly pure, the melting point is raised and it begins to form pasty masses. These are raked to

the door of the furnace, removed and hammered or rolled into shape. Small amounts of slag remain with the iron, giving it a fibrous structure which makes it tough and flexible.

Wrought iron can be easily welded and forged. It is used in the manufacture of chains, anchors, bolts, rivets and for general blacksmith work.

451 Steel

Steel is a compromise between pure iron and cast iron, and its properties depend on two factors, carbon content and heat treatment subsequent to its manufacture. This heat treatment accompanied by mechanical treatment influences the physical structure and hence the physical properties of the final product.

Its low carbon content (0.02 to 0.8 per cent) as compared with that of cast iron (3 to 4 per cent) gives steel great tensile strength. It does not melt sharply as cast iron does, but softens, so that it can be rolled while hot into rails and structural steel generally.

Ferrous alloys occupy a very large place in modern metallurgy because of their special properties. If the carbon content, for example, does not exceed 1.5 per cent, the effect of adding metals may be stated briefly as follows. About 13 per cent of manganese donates hardness to the steel, the same effect being given by smaller amounts of tungsten or molybdenum; nickel, 3 to 40 per cent, adds great toughness—hence its use in the armor of modern warships (Harveyized Steel); nickel and chromium produce a tough, hard and stainless steel when in the percentages of approximately 10 and 20, respectively.

High-speed steels which retain their properties at red heat contain up to 20 per cent of tungsten, about 5 per cent of chromium and small quantities of other metals. Modern vehicles of transportation and the machinery used in their manufacture rely increasingly on nickel, chromium, manganese and tungsten. Canadian resources and output of nickel are practically the entire world supply of this metal. Forty per cent of the world's chromium comes from Southern Rhodesia and the Union of South Africa, the rest being produced mainly by Russia and Turkey. Russia controls one half the manganese of the world, with India a close competitor. Of the tungsten supplies, one third comes from India, one third from China and one third from the United States.

452 The Electric Furnace

This type of furnace resembles the open hearth. Heat is generated by means of an electric arc, and the furnace has a basic lining. There is no oxidizing flame as in the open hearth, and the heat can be carefully regulated so as to produce a high-quality steel from rather low-grade ores. Such a furnace has a capacity of three to fifteen tons.

453 Heat Treatment of Steel

(1) *Tempering.* The carbon in steel is present in the form of iron carbide (Fe_3C). At high temperatures this is in solution in the iron. If the steel is allowed to cool slowly some of the iron carbide comes out of solution as crystals. If, however, the steel is cooled suddenly the crystals do not have time to form. The percentage of iron carbide in solution governs the hardness of the steel. If the steel is cooled slowly it is soft, while it is at its hardest if it is cooled suddenly by quenching in water or oil.

The process of tempering consists of heating the steel, then allowing it to cool to a certain temperature before quenching. At different temperatures the steel assumes a characteristic color, which is sometimes used as a guide in tempering tools.

(2) *Case Hardening.* Sometimes steel needs to be tough and malleable in order to have the necessary strength, but the outside surface must be hard in order to present a hard-wearing surface. Such a condition is necessary in gears for motor cars or in table knives. Articles of this kind are made of a mild steel (low carbon content) and then packed in charcoal and heated. The carbon slowly penetrates the steel at the surface, giving the outer surface of the article a hard layer of high carbon steel. The process is known as case hardening.

454 The Smelting of Copper

Copper is smelted chiefly in reverberatory furnaces. In some processes sulfide ores are first partially or completely oxidized in a roasting or sintering furnace. The ore and flux are fed to the reverberatory furnace and the sulfides melt, so that a mixture of sulfides of copper and iron, called a *matte,* is produced. This matte is then treated with air in a copper converter analogous to a Bessemer converter, where the iron is oxidized and formed into slag and the copper is reduced to a metal known as *blister* copper. The

copper may now be further refined by heat or cast into anodes for electrolytic reduction. If the ore contained gold or silver, the metals are retained in the blister, and may be recovered as a sludge in the electrolytic tanks along with other elements such as selenium and tellurium.

Lead is reduced in one stage in a blast or reverberatory furnace. In one process zinc ore is packed along with carbon into crucibles and the metal distilled out. Nickel is associated with copper in many ores, and its treatment is therefore similar to that of copper.

Alloying materials such as ferrosilicon, ferrochromium, ferrotitanium, ferromanganese and ferrotungsten are reduced in electrical furnaces. The high cost of electric furnace operation prevents its use for less drastic reductions, although it is used in the direct process for steel making, where only small amounts of steel are required.

455 Electrolytic Refining

Copper and nickel are examples of metals which may be deposited from aqueous solution by the electric current. Roasting and carbon reduction produce a copper blister of about 98 per cent copper with small quantities of gold, silver and other metals present. Plates of this metal are made the anodes in a large number of cells containing an aqueous solution of copper sulfate; the cathodes are thin sheets of pure copper. The passage of a direct current causes pure copper to be deposited on the cathodes while the anode is disappearing into solution. By this means a practically pure cathode known as electrolytic copper is built up. Impurities such as gold and silver are precipitated to the bottom of the cells and later recovered. The reactions involved may be expressed as follows:

$$\text{At the anode, } Cu - 2e \rightarrow Cu^{++} \tag{153}$$

$$\text{At the cathode, } Cu^{++} + 2e \rightarrow Cu \tag{154}$$

456 The Preparation of Metals from Fused Compounds

Some metals, especially those high in the electromotive series, are not readily obtained from their compounds by carbon reduction. For the small-scale production of some metals powdered aluminum may be used. The basis of its usefulness is the great

heat of reaction evolved when aluminum unites with oxygen:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 760{,}000 \text{ calories} \qquad (155)$$

This attraction for oxygen can be utilized by igniting a mixture of powdered aluminum and iron oxide (a mixture known as thermite). A vigorous reaction occurs, producing a temperature of over 2000°C, reducing the iron oxide to molten iron and setting free light alumina which is blown away.

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \qquad (156)$$

A mixture of aluminum and iron oxide is called *thermite*, and this method of release of iron or other metal from its oxide is called the *Goldschmidt* process.

None of these methods so far described is suitable for the preparation of the alkali and alkaline earth metals, magnesium and aluminum. For their preparation we use electrolysis of the fused compounds.

457 Preparation of the Alkaline Earth Metals

The preparation of calcium illustrates a method which is applicable to strontium, barium and other metals of their type. The electrolytic cell used is a graphite crucible which serves as the anode. In it is placed anhydrous calcium chloride. The cathode is a copper rod usually tipped with iron. The electric current melts the calcium chloride and, as the cathode is slowly raised, metallic calcium adheres to it. Thus a rod of calcium is obtained with a thin coating of fused calcium chloride which protects it from the atmosphere. It is now ready for scaling and packaging in air-tight containers. The equation is

$$E + CaCl_2 \rightarrow Ca + Cl_2 \uparrow \qquad (157)$$

458 Preparation of the Alkali Metals

Sodium, the commonest of the alkali metals, is prepared by electrolysis of (*a*) its fused chloride and (*b*) its fused hydroxide.

(*a*) *From its fused chloride.* The melting point of sodium chloride is 805°C, but may be lowered considerably by the addition of small amounts of other chlorides. An iron cell of cylindrical shape is used, and the cathodes, radially grouped, are of iron. The anode, centrally placed, is of graphite. The cell is partially filled with dry

sodium chloride or its mixture with other compounds. When the chloride is fused, liquid, metallic sodium is attracted to the cathodes at the sides. Here it floats above the molten mass and is drawn off at intervals to be packaged in airproof containers. The chlorine gas is liberated at the central anode and passes off through a shield which protects it from contact with the molten sodium. The equation is

$$E + 2NaCl \rightarrow 2Na + Cl_2 \uparrow \tag{158}$$

(*b*) *From its fused hydroxide.* Sodium hydroxide is more easily fused than the chloride and is often used as an alternative. The process is very similar to the one described in (*a*) except that oxygen is liberated at the anode and hydrogen accompanies sodium to the cathode. The molten sodium, protected from air by a layer of hydrogen, is tapped off at intervals and stored as previously stated.

$$E + 2NaOH \rightarrow 2Na + H_2 \uparrow + O_2 \uparrow \tag{159}$$

459 Preparation of Magnesium

Magnesium was first prepared by Davy in 1808. He originated the method of preparation of metals (Li, Na, K, Ca, Mg) from their fused compounds by means of a direct current of electricity. This method did not produce pure magnesium because of the retention of water by the electrolyte even at high temperatures. During recent years the advent of cheap electrical power has simplified this process and made available at very low cost both magnesium and aluminum.

In the modern Dow process sea water is the source of magnesium. Magnesium hydroxide is precipitated by the addition of lime obtained from calcium carbonate (sea shells):

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 \downarrow \ CaCl_2 \tag{160}$$

The addition of hydrochloric acid to this precipitate forms the chloride

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O \tag{161}$$

This magnesium chloride, when freed from water and dried thoroughly, is melted and electrolyzed. Molten magnesium floats to the top of the molten salt and is dipped off as required. Chlorine is released at the anode and may be collected. The process is not unlike that for the production of sodium or calcium from the chloride.

Another process makes use of dolomite, a common, naturally occurring mixture of calcium and magnesium carbonates. When this ore is heated carbon dioxide is evolved, and a mixture of the oxides of calcium and magnesium results. These mixed oxides are then heated in an electric furnace with ferrosilicon. The high temperature involved causes the magnesium to volatilize; meanwhile the calcium and silicon unite to form calcium silicate, the iron not entering into the reaction:

$$2(CaO \cdot MgO) + Si \rightarrow Ca_2SiO_4 + 2Mg\uparrow \qquad (162)$$

460 Preparation of Aluminum—the Hall Process

Although first isolated in 1825, it was not until 1886 that aluminum was manufactured on a sufficiently large scale to make it

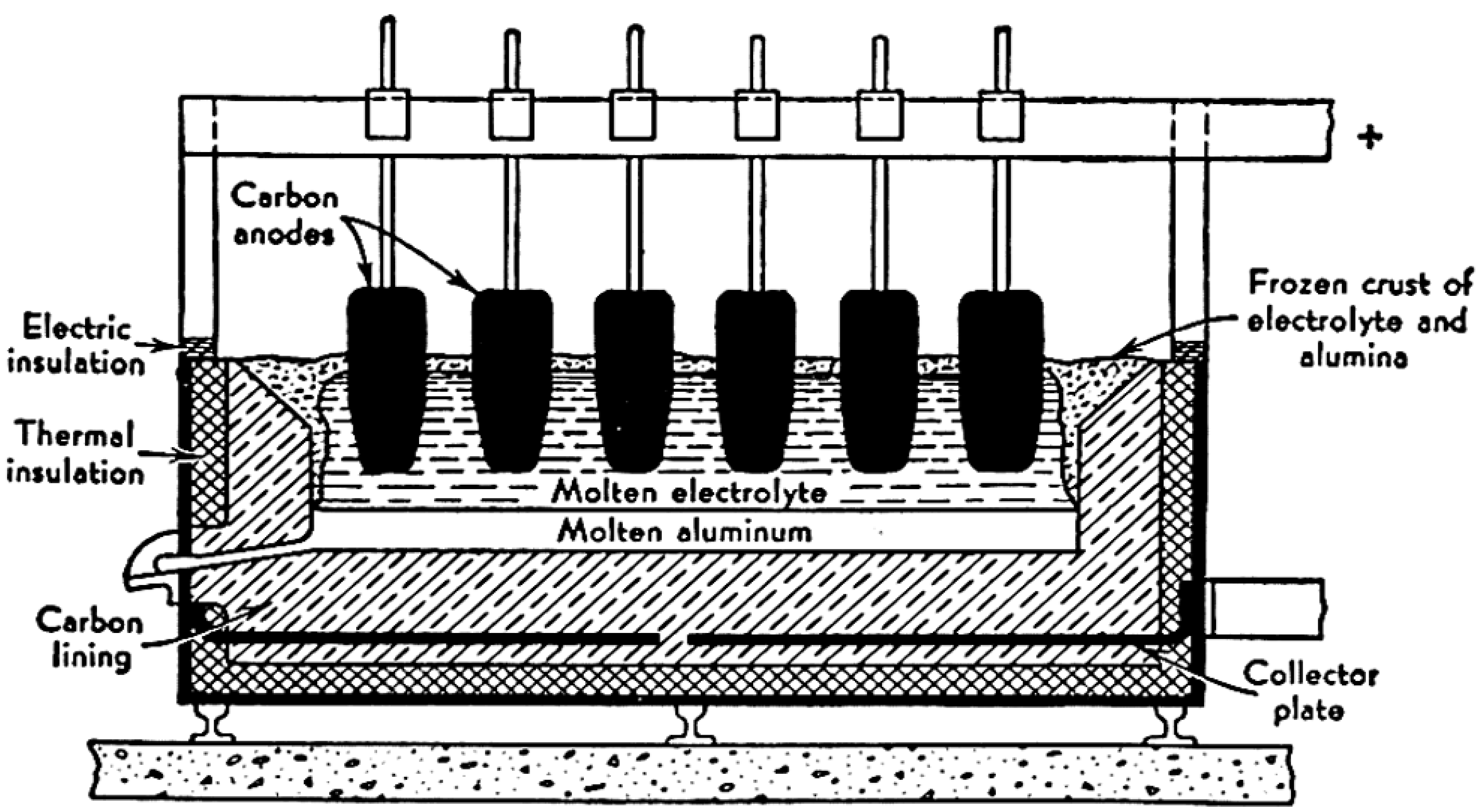


Fig. 77. Diagram of a furnace for making aluminum by the Hall process.

available at low cost. In that year it was prepared simultaneously by Heroult of France and Hall of the United States, when both were about twenty-two years of age.

The raw materials used are cryolite (Na_3AlF_3) and bauxite. Bauxite, which is obtained chiefly from British Guiana, contains salts of iron and titanium as impurities. It is purified by treating the crushed bauxite with a concentrated solution of sodium hydroxide, forming soluble sodium aluminate ($NaAlO_2$). The impurities are removed by filtration. The filtrate is then treated with excess water; this precipitates aluminum hydroxide. On heating, the water is driven off and pure Al_2O_3 results.

A high-grade cryolite or similar mixture of fluorides serves as the solvent for aluminum oxide in the electrolysis.

The apparatus consists of an iron cell lined with coke, which serves as the cathode. The anode is a number of carbon rods. A charge of Al_2O_3 and crushed cryolite is put into the cell, and the current is turned on. The heat generated melts the cryolite which helps to lower the temperature required for electrolysis. As the Al_2O_3 is decomposed (equation 92), the molten aluminum sinks to the bottom and is drawn off as required. At the same time a further charge of Al_2O_3 is added, keeping the process continuous (Fig. 77).

Theoretically this process could go on indefinitely if it were not for the destruction of the anode by the nascent oxygen (equation 93).

461 Summary

Metallurgy is the science of recovering metals from their ores and the study of these metals. The classical method of metallurgy is the treatment of ores at high temperatures; this is pyrometallurgy.

The heat treatment of iron ores involves chemical reduction by carbon and carbon monoxide. This reduction is effected by heating with coke, as in the blast furnace where the combustion of carbon supplies the heat and reduction.

To rid the molten metal in a furnace of infusible materials a flux is added, which causes the silica, etc., to flow so that it may be removed as slag.

The product of the blast furnace when iron is smelted is cast iron. Reduction of the carbon to a low value gives mild steel, whose properties may be enhanced by alloying with manganese, chromium, nickel, tungsten, etc.—the ferrous alloys.

Copper ores are first roasted to change the sulfide to oxide and then reduced. Refining is effected by electrolysis. Small quantities of gold and silver may be recovered from the electrolytic bath. Electrical methods are gradually replacing pyrometallurgy.

Electrolysis is the decomposition of chemical compounds by the electric current.

Compounds of copper, silver, gold and nickel are readily decomposed to give up their metals to the cathode in aqueous solution.

For metals not easily reduced from their oxides, aluminum may be employed. Aluminum powder combines with the oxygen to form alumina (Al_2O_3) and release the molten metal.

Such metals as aluminum, calcium and sodium do not so deposit from aqueous solution, but from their molten compounds. With calcium and magnesium the chlorides are used, the metals being deposited at the cathode and chlorine passing off at the anode.

Sodium may be prepared either from its fused chloride or, at a lower temperature, from its fused hydroxide.

Another method of preparing magnesium is by fusion of its mixed oxide (with calcium) and ferrosilicon.

To prepare aluminum purified bauxite is fed into a bath of molten cryolite and there electrolyzed.

Questions

1. What do you understand by the term metallurgy? What is pyrometallurgy?
2. Name and describe briefly the various types of furnaces used in pyrometallurgy.
3. Describe briefly the smelting of iron.
4. What is steel? What factors are involved in the production of steel alloys?
5. Of what importance is the lining of a furnace?
6. How is copper refined and what are the possible by-products?
7. What are (*a*) the chief uses and (*b*) the unfavorable properties of cast iron?
8. What are (*a*) tempering and (*b*) case hardening as applied to steel?
9. Outline the various factors which must be considered before deciding to manufacture a newly discovered product.
10. What is the Goldschmidt process?
11. Outline a general procedure for the preparation of a metal by electrolysis of a fused compound of that metal.
12. How does the Hall process differ from your outline given in question 11?

33

Industries Based on Coal

462 Coal

In spite of the recent advances in the development of water power as a source of energy of all kinds, coal still remains our major raw material for this purpose. Subsidiary to it is petroleum, while wood is used in localized areas for the production of heat. Together these three raw materials represent far more to the chemist than sources of heat energy. Coal in its several varieties consists of the decomposition products of wood of bygone ages resulting from the effects of extreme heat and pressure. It is possible to trace this historical process by reference to Table 43. This table shows

TABLE 43

THE GEOLOGICAL STORY OF COAL PRODUCTION

Type	Composition of Type Samples					Fuel Value
	H_2O	Ash	H	C	O	
Wood—air dry	11.36	0.27	5.35	44.13	38.83	4242
Peat—Wis.	76.94	3.99	1.02	10.87	6.33	1044
Lignite, brown—Colo.	34.40	13.89	2.64	35.94	12.33	3364
Lignite, black—Colo.	18.94	6.29	3.60	57.47	12.23	5401
Bituminous—Ill.	9.94	8.84	4.24	66.18	8.06	6508
Bituminous—W. Va.	2.44	6.34	4.96	77.90	5.87	7721
Semibituminous—W. Va.	2.80	6.48	4.26	81.75	2.66	7923
Semianthracite—Pa.	3.16	10.17	3.12	79.49	2.29	7431
Anthracite—Pa.	3.33	9.12	2.71	81.35	2.10	7417
Charcoal	.....	2.43	1.49	82.05	14.01	6626
Coke	.....	12.89	0.58	83.16	2.45	6768

the percentage composition of wood, followed by peat down to anthracite, with charcoal and coke shown for comparison. These percentages do not add up to 100 because the small amounts for nitrogen and sulfur, never exceeding 1.6 per cent, have been omitted. The last column shows the fuel values in calories per gram.

A glance at Table 43 shows that the effect of heat and pressure on the buried woods of the Carboniferous Era was to "squeeze out" those constituents represented in the analysis by H_2O—the formula for cellulose is $(C_6H_{10}O_5)_n$—thereby increasing the percentage of pure carbon. Consequently, the ratio of carbon to the other constituents rises and with it the heat or fuel value.

The first stage of this decomposition might be represented by a muck soil. Peat, a further stage in time, is used as a fuel in the absence of something better. Lignite contains a higher percentage of free carbon and is also an inferior type of fuel. Bituminous or soft coal is a better grade of fuel but burns with a great deal of smoke. It contains a fairly high percentage of volatile matter which is driven off when the coal is heated in the absence of air. The anthracites and hard coals represent the most advanced stages of decomposition of the vegetable matter. They are usually found deeper in the earth and hence have been subjected to greater pressures.

463 Destructive Distillation of Coal

The destructive distillation of coal was first utilized about two centuries ago to provide gas for illuminating purposes, and it was not until over a hundred years later that the other products received consideration. The type of coal most suitable for this treatment is a bituminous variety, which at 1000°C swells and gives rise to a porous, hard carbon known as coke and to a large variety of gases and liquids. The yield of coke approximates 70 per cent of the weight of the coal, the other 30 per cent being coal gas, ammonia, light oils and tar. A simple diagram is shown in Fig. 78.

Purified coal gas is about one half hydrogen, one third methane and the rest the carbon oxides, oxygen and nitrogen. The increased use of electricity has decreased the value of coal gas as an illuminant, so that it is now more generally used for heating purposes.

As distillation proceeds, the complex structure of the coal yields

products which, unlike coal gas, may be readily condensed. The lower boiling fractions of this condensate contain benzene, toluene, etc.—all liquids—followed later by naphthalene, anthracene, phenol and, last, by tar and pitch. The former compounds find application in the manufacture of dyes, pharmaceuticals and explosives; tar and pitch are used mainly for waterproofing and road making.

Though the principles of destructive distillation are the same whatever the conditions, the different temperatures at which coal

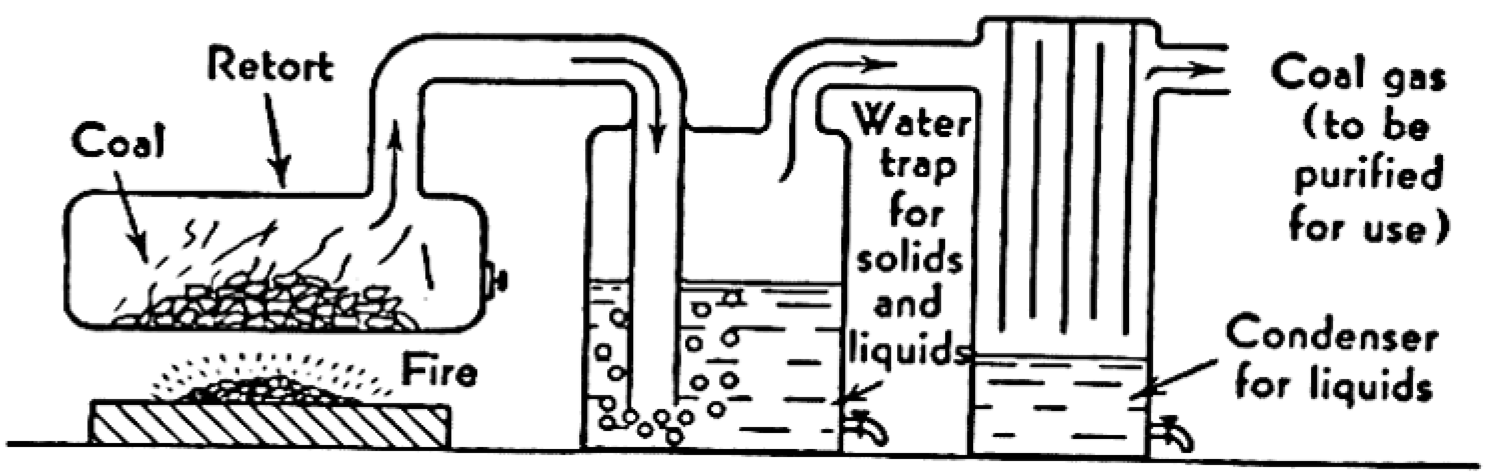


FIG. 78. Illustrating the destructive distillation of coal.

may be heated show a variation in the kind and quantity of products obtained. Thus under 600°C less aromatic hydrocarbons, for example, benzene and toluene, are given off; but they appear if the temperature of distillation is kept at 800°C. A temperature between 800° and 1000°C is best for the production of coke, whereas at a temperature 200°C higher the best yields of coal gas are obtained.

464 Coke

The coke required for metallurgical purposes must be so dense and hard as to offer strenuous resistance to crushing. Only special kinds of coal produce a product suitable for this use. In particular, a good gas coal does not produce a proper metallurgical coke, and so the two processes of coal distillation cannot be combined to serve both ends. If this operation is carried on at a temperature of 500° to 700°C, a partial coke product is obtained which still contains a large percentage of volatile matter and serves as an excellent domestic fuel. The liquids which distill over from this low-temperature process may be later treated to serve as a good motor fuel.

Coke may contain 5 to 20 per cent of inorganic material (ash), depending on the quality of the coal from which it was made. An

undue quantity of sulfur in this ash unfits it for many uses. The chief use of coke is in the reduction of metallic ores. Its next most important use is as a fuel when anthracite is unobtainable. Also, by strongly heating in the electric furnace, it is convertible into *synthetic graphite*. A ton of coal normally yields 1200 to 1500 pounds of coke, 120 pounds of tar and 12,000 cubic feet of gas.

The gaseous fraction from coal consists chiefly of hydrogen and methane (CH_4), which together make up 80 per cent. The rest is ethane (C_2H_6), ethylene (C_2H_4), carbon monoxide and dioxide and nitrogen. Before being purified, coal gas contains quantities of hydrogen sulfide; but by passage over trays of iron oxide this bad-smelling component is removed.

Because of its high content of methane (30 per cent), coal gas when burning shows a highly luminous flame produced by the carbon particles. The flame of burning hydrogen is colorless and that of carbon monoxide is almost so. As seen above, a large weight of coal produces a rather small yield of gas. Means have been found to utilize some of the coke, produced at the same time as the gas, to increase the supply of gas for heating purposes. These means take the names of *water gas*, *producer gas* and *blast furnace gas*.

465 Water Gas

It is prepared by passing steam over hot coke:

$$28{,}300 \text{ calories} + H_2O + C \rightarrow CO + H_2 \qquad (163)$$

and the resulting mixture is called water gas. It is approximately 50 per cent hydrogen and 40 per cent carbon monoxide. If water gas is to be used for lighting purposes, it must have some hydrocarbon gases mixed with it in order to give it a luminous flame. This process is called *enriching*.

466 Producer Gas

This gas is used chiefly in metallurgical processes for the operation of blowing engines. It is made by forcing air through deep beds of hot coke or coal. The oxygen of the air partially oxidizes the carbon to form carbon monoxide, which is the chief constituent of producer gas.

$$2C + O_2 \rightarrow 2CO \qquad (164)$$

Since the air contains about four fifths nitrogen, this gas will also be found in the resulting mixture. The presence of this much nitrogen greatly lowers the fuel value of the gas. Some steam is often forced in with the air and is reduced in the same manner as in the manufacture of water gas.

467 Blast Furnace Gas

It is obtained as a product of the furnaces used in the extraction of iron from its ores. The product is a mixture of carbon monoxide, carbon dioxide and nitrogen, and is similar in composition to producer gas. It is extensively used in the iron and steel plants as a fuel for heating the stoves in which the air for the blast furnace is preheated and in the operation of gas engines.

Table 44 shows the composition of a number of industrial gaseous fuels, including natural gas.

TABLE 44

COMPOSITION OF SOME INDUSTRIAL FUEL GASES

	Natural Gas	*Coal Gas*	*Enriched Water Gas*	*Producer Gas*	*Blast Furnace Gas*
CH_4	92.5	30.0	10.0	4.0	0.2
C_2H_6	0.5	3.0	3.0	....	....
C_2H_4, etc.	0.5	4.0	14.0	....	....
H_2	2.2	50.0	37.0	10.0	3.0
CO	0.5	9.0	30.0	25.0	27.0
CO_2	0.3	1.0	3.0	5.0	12.0
N_2	4.0	3.0	3.0	56.0	57.8

468 Evaluating a Fuel

The heat or calorific value of a fuel is based upon the calorie (see § 393), which is the quantity of heat required to raise 1 gram of water 1° in temperature on the centigrade scale. However, for most practical measurements, the British thermal unit (Btu) or some variation of it is preferred. *One Btu is the amount of heat required to raise 1 pound of water 1° in temperature on the Fahrenheit scale.* One pound is equal to 454 grams—a large value; but 1°F is only five ninths of 1°C. One Btu, therefore, is equal to five ninths of 454 calories, that is, 252 calories. To change Btu to calories we therefore multiply by 252; to change calories to Btu, we divide by 252, or multiply by 0.00397.

In Tables 45 and 46 we see the fuel values in Btu for some commonly used fuels.

TABLE 45

FUEL VALUES OF SOME COMMON LIQUID FUELS

Liquids	*Fuel Value (Btu per pound)*
Gasoline	20,000
Kerosene	20,000–21,000
Benzene	18,000
Methyl alcohol	9,550
Ethyl alcohol	12,780

TABLE 46

FUEL VALUES OF SOME COMMON SOLID FUELS

Solids	*Fuel Value (Btu per pound)*
Wood and cellulose	6,500– 7,800
Peat	7,800–11,500
Brown lignite	11,500–13,000
Black lignite	13,000–14,000
Bituminous coal	14,000–16,000
Semi-anthracite	15,500–16,000
Anthracite	15,000–15,500

469 Calcium Carbide

Within recent years acetylene has come to be regarded as one of the chief raw materials in the manufacture of carbon compounds, probably ranking third with coal and petroleum. Calcium carbide stands at the crossroads between inorganic and organic chemistry since it is formed from limestone and, through acetylene, gives rise to an incalculable number of carbon compounds.

In essence the formation of calcium carbide is effected by the high temperature fusion of lime and carbon:

$$CaO + 3C + 121{,}000 \text{ calories} \rightarrow CaC_2 + CO \qquad (165)$$

This endothermal reaction requires a high temperature, and the carbide produced is a highly endothermal body. It is a dull gray, somewhat porous solid. In practice a mixture of lime and crushed coke is fed continuously into an electrical arc furnace. The molten carbide quickly solidifies, and is raked away and packed in airtight containers.

The raw materials required are coke and a high grade of lime obtained by heating limestone. The limestone should be free from

phosphate so as not to cause the formation of phosphine when calcium carbide is treated with water. The reaction with water to produce acetylene is

$$CaC_2 + 2H_2O \rightarrow C_2H_2 \uparrow + Ca(OH)_2 \qquad (166)$$

470 The Cyanamide Process

This process is worked extensively on this continent and is one sequel to the large-scale production of calcium carbide. If calcium carbide (CaC_2) is heated in an atmosphere of nitrogen at about 1000°C, a reaction ensues with the formation of calcium cyanamide:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \qquad (167)$$

This compound, which is not to be confused with calcium cyanide [$Ca(CN)_2$], is very often used as a fertilizer. It is a valuable source of ammonia, for it reacts with water, at a pressure of 50 to 60 pounds per square inch, in the following manner:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3 \qquad (168)$$

471 Other Carbides

If for the lime used in the manufacture of calcium carbide. silica (SiO_2) is substituted, silicon carbide is produced:

$$SiO_2 + 3C \rightarrow SiC + 2CO \uparrow \qquad (169)$$

It is a very hard solid formed as iridescent black crystals, widely used as an abrasive, replacing many natural materials previously so used. The carbides of tungsten (W_2C), boron (B_4C) and iron (Fe_3C) are likewise very hard.

472 Summary

Plant life of the Carboniferous Era has left us large deposits of coal of various types; their history can be traced from peat to anthracite.

Destructive distillation is the term applied to the heating (out of contact with air to avoid combustion) of materials of complex structure in order to obtain simpler products (compare with cracking).

The destructive distillation of coal leaves behind a residue of coke which is about 70 per cent of the coal. The rest distills over and consists of gases, liquids, solids and tar. Different temperatures produce a different ratio of these products.

The liquid portion contains benzene, toluene, etc.; among the solids are naphthalene, anthracene and phenanthrene in small quantities.

Coke may be used (1) in metallurgy, (2) as a fuel, (3) to prepare fuel gases such as water gas and producer gas.

Fuels, whether solid, liquid or gas, are evaluated for their output of heat by combustion with oxygen under controlled conditions. One Btu = 252 calories.

The manufacture of calcium carbide is another example of reduction which has drawn a great deal of attention to itself in the last three decades. This reduction takes place between carbon and lime in the electric arc. The product is used either for the subsequent manufacture of calcium cyanamide or for the preparation of acetylene as a raw material for chemical synthesis.

Calcium cyanamide is made by heating calcium carbide in an atmosphere of nitrogen at about 1000°C. When the resulting product is treated with water, ammonia is liberated and calcium hydroxide is left behind. This makes calcium cyanamide available as a fertilizer to maintain a sufficiency of lime and ammonia in the soil.

Several other carbides, notably those of silicon, boron, iron and tungsten, are very hard. They can be prepared in a manner similar to that used for calcium carbide. All these carbides except that of calcium are very hard and may be used as abrasives.

Questions

1. Name the various stages by which coal may be considered to be derived from wood.
2. Define destructive distillation. Name the types of substances obtained in the destructive distillation of coal.
3. How does changing the temperature of a coke oven affect the products?
4. Name the principal uses of coke.
5. What is meant by the "enriching" of coal gas?
6. What is the relation between the calorie and the Btu?
7. Outline the process for the production of calcium carbide. Why is this compound important in industry?
8. Do you see any advantage to the consumer of a fuel if he paid for it according to its Btu's?

34

Industries Based on Wood

473 Wood

All plant life contains the insoluble polysaccharide cellulose, the extent to which it exists in any one species being to some degree associated with the height and strength required to withstand the effects of climate. In this respect cellulose is to the plant what the bony skeleton is to vertebrate animals. But, in addition to this feature, cellulose is the basis of the fibrous structure which surrounds the individual cells of plants; here the fibers of cellulose are bound together by lignin, another complex carbon compound, which serves as a cement. Cellulose is likewise found in the covering of grains and in a pure form as cotton of the cotton plant.

The first industrial use of cellulose is credited to the Egyptians, whose papyrus of beaten reeds bears the same legend found in our word paper. Ever since the cultivation of the cotton plant, especially in the southern United States, cotton has been used for weaving cloth and for making paper. Cotton has now become an international commodity of importance, and attempts—some successful—have been made to grow it in various parts of the world, notably in Egypt, Russia and China.

In recent years the cellulose of wood, and more particularly the soft woods such as spruce and fir, has been utilized to an increasing degree in the manufacture of those products previously prepared from cotton, if prepared at all.

474 Destructive Distillation of Wood

This process has lost its significance since more modern methods have appeared for the production of methyl alcohol and acetic acid. Originally wood was destructively distilled for the charcoal which is left behind, but this was a wasteful procedure. The type

of apparatus required is simple, consisting of an iron retort with a door by which the charge may be added and an exit pipe for gases and other volatile matter. Attached to this pipe is a series of condensers to catch all condensable materials which may be driven over (Fig. 78). Heating drives off a variety of gases of greater or lesser complexity and leaves behind the soft, black, porous solid known as *wood charcoal.*

By this treatment different woods tend to produce different products. Soft woods, such as pine, contain, besides cellulose, considerable quantities of rosin and turpentine, and it is chiefly for these that wood distillation plants are operated. In addition to them, some methane and ethane are produced as well as methyl alcohol and acetic acid, these last constituting the crude distillate known as *pyroligneous acid,* which is soluble in water. Hard woods, such as beech, birch, ash, etc., contain less of volatile oils; and during the heating from about 250° to 400°C, gases are at first evolved, followed later by light and then by heavier oils. These gases consist mainly of carbon dioxide, carbon monoxide, methane and other simple hydrocarbons. The liquids evolved are condensed, the lighter fractions containing chiefly acetic acid and methyl alcohol. The higher boiling fractions consist of wood oils, creosote, tar and pitch. The residue is charcoal. These products have varied industrial uses.

475 Newsprint

The largest consumption of wood cellulose is in newsprint and similar products, and for this purpose there are two general methods of treatment—the mechanical and the chemical. In the mechanical treatment wood is ground up to a meal (ground pulp) and then pressed into the desired shape and thickness of the product demanded. Grinding produces very short fibers, and the mechanical strength of the product is not great.

476 Sulfite Pulp

The chemical treatment of wood utilizes fairly large chips which may be put through one of three processes, the commonest being known as "sulfite cooking." By this method wood chips are boiled up in an aqueous solution of lime and sulfur dioxide. These two reagents form calcium bisulfite [$Ca(HSO_3)_2$], the product of the treatment being a relatively pure cellulose. Lignin and resinous

materials present in the original wood are retained in the cooking liquor when the "cook," as it is called, is screened and washed. The bleaching of this product is usually carried on by treatment with a hypochlorite or chlorine. When washed and pressed the cellulose is ready for drying in sheets or for any other treatment to prepare it for its final use. When dry it is comparable with cotton, except that the fibers are shorter.

477 Cellulose Nitrate

The preparation of nitrates of cotton for explosives opened the way to further development of the chemical treatment of cellulose whether as cotton or as prepared wood pulp. The action of nitric acid, in the presence of sulfuric acid, is to form one or more nitrates by reacting with the free hydroxyl groups which exist in cellulose. Cellulose may be considered to have to some extent the structure of glucose ($C_6H_{12}O_6$), many molecules of glucose being linked together in such a way as to leave three exposed OH groups per $C_6H_{10}O_5$ unit of cellulose. In this way it is possible to suggest this simple scheme:

$$[C_6H_7O_2(OH)_3]_n + 3nHNO_3 \rightarrow [C_6H_7O_2(NO_3)_3]_n + 3nH_2O \quad (170)$$

This is cellulose nitrate, commonly but incorrectly called nitrocellulose and frequently referred to as *guncotton* from its use as a propellant.

478 Nobel's Explosive

Cellulose nitrate is soluble in a variety of organic solvents such as acetone, from which it may be regained by evaporation. The discovery by Nobel (1889) that a mixture of cellulose nitrate and glycerol trinitrate gave rise to a plastic material that could be molded brought about the use of this mixture as an explosive that would react more slowly—hence less disastrously—than glycerol trinitrate alone. This mixture is dissolved in acetone and the solution extruded in such a manner as to evaporate the solvent acetone and produce thin cords—hence the name *cordite*.

479 Pyroxylin

In the nitration of cellulose to produce the cellulose trinitrate described above, the trinitrate shows by analysis a nitrogen content

of 14.14 per cent. If cellulose is nitrated so as to contain a smaller percentage of nitrogen (about 11), the product obtained is called *pyroxylin*. Collodion, which is a solution of pyroxylin in a mixture of alcohol and ether, is useful for a variety of purposes, such as covering up cuts and mending typed stencils. On exposure to the atmosphere the ether and alcohol evaporate, leaving a dry, hard film which is waterproof. Pyroxylin finds industrial application in many other directions; dissolved in camphor it constitutes celluloid, which can be incorporated with various coloring matters and made into a variety of useful and ornamental materials.

But the film of pure pyroxylin is hard and likely to crack, not giving the flexible covering characteristic of paints containing linseed or tung oil. To overcome this disadvantage and still utilize the waterproof nature of pyroxylin, it is dissolved in solvents such as butyl or amyl acetate ($CH_3COOC_4H_9$ and $CH_3COOC_5H_{11}$) and mixed with some liquid which will not evaporate along with these esters after the whole is allowed to dry. This added liquid is known as a *plasticizer*, that is, it renders the final film plastic or capable of molding. This is the basis of pyroxylin lacquers which, when suitably colored, compete seriously with ordinary paints. In addition, solid pyroxylin when plasticized may be molded and cut into a great variety of useful products such as combs and brushes.

480 Cellulose Acetate

Photographic films may also be made of pyroxylin. They have, like all cellulose nitrate bodies, one disadvantage—their inflammability. Of late years cellulose acetate has to a large extent replaced these nitrates for finishes and molded objects. If cellulose is treated with acetic anhydride and sulfuric acid, it is possible to attach three acetate ($CH_3COO—$) radicals to each glucose unit of the cellulose. It may be represented simply as follows, with acetic acid (CH_3COOH) used in place of acetic anhydride [$(CH_3CO)_2O$]:

$$[C_6H_7O_2(OH)_3]_n + 3nCH_3COOH \rightarrow [C_6H_7O_2(CH_3COO)_3]_n \quad (171)$$

This cellulose acetate is soluble in acetone and, like cellulose nitrate, may be made to furnish lacquers, films and molded objects. Again, a plasticizer is desirable to prevent cracking and permit of

molding and working with tools. In addition, cellulose acetate lends itself to the manufacture of artificial silk.

The chemical treatment of cellulose is one of the outstanding industrial developments of this century, providing as it does such products as those mentioned above as well as the huge quantities of chemical wood pulp which go into the production of newsprint and allied industries.

481 Artificial Silks

But the most interesting developments relating to cellulose, whatever its source, have been those designed to replace natural silk. Natural silk is of animal origin and therefore similar to wool in that both belong to the class of bodies known as proteins and contain a considerable proportion of combined nitrogen as well as small quantities of combined sulfur. Cellulose, on the other hand, is a carbohydrate and is more resistant to the action of chemical reagents, heat and insects such as moths. Silk and wool must always be more expensive than cellulose because of the food that the silkworm requires in proportion to the quantity of silk produced and because of the acreage necessary for the feeding of sheep. The supply of cellulose is not limited to cotton and wood fibers, for it may be obtained from many types of agricultural refuse such as straw and cornstalks. Moreover, by a policy of reforestation, the present wooded areas, such as those of Maine, Quebec and New Brunswick, may be made to produce wood for cellulose manufacture indefinitely. The so-called artificial or synthetic silk industry produces not merely a substitute for silk but also several varieties of goods that in the main can be said to be superior to silk.

There are four types of artificial silk, depending on the mode of manufacture. They are described briefly here.

482 Viscose

In the viscose process a good quality of cellulose, such as bleached sulfite pulp, is treated with an 18 per cent solution of sodium hydroxide. This is pressed free of solution, shredded and treated with carbon bisulfide, which produces the sodium salt of an acid of sulfur and cellulose, sodium cellulose xanthogenate. This is a thick, viscous, colloidal solution—hence the term *viscose*. After standing awhile, this liquid is forced through tiny holes into a dilute solution of sulfuric acid, which neutralizes and decomposes

the alkaline xanthogenate, producing, from each tiny hole, a somewhat sticky thread of cellulose. This thread soon hardens in the acid bath and, while wet, is wound on spools. These spools are put in a drier and the threads later re-wound; they are now ready, after appropriate dyeing, for spinning. By varying the diameter of the holes through which the viscose is forced, threads of different sizes can be obtained.

This type of artificial silk, generally known as *rayon*, can be produced in both the dull and the glossy finish. It is very strong and wears well; it likewise takes on a great variety of colors when suitably dyed.

483 Mercerized Cotton

This product is obtained when cotton is treated with a concentrated solution of alkali. It forms a sodium salt of cellulose which, when washed and dried, has a somewhat glossy finish resembling silk more than does ordinary cotton.

484 Regenerated Cellulose

Cellulose may be dissolved in Schweitzer's reagent, obtained by adding an excess of ammonium hydroxide to a solution of copper sulfate. Here a complex of some sort is formed which may be decomposed by the addition of sulfuric acid; this precipitates (or regenerates) the cellulose and produces a high grade of artificial silk.

485 Chardonnet Silk

Nitro silk, as it is often called, is prepared by an old process, that of Chardonnet. It consists of dissolving pyroxylin in alcohol and ether and forcing the resulting solution through fine capillaries into either water or air. In the air the solvents evaporate, whereas in water the pyroxylin is precipitated. In either instance threads of cellulose nitrate are produced. They are, of course, inflammable; but, when treated with a solution of sodium sulfide, the nitrate radicals are removed, leaving a hydrated cellulose of good quality.

486 Cellulose Acetate Silk

The most recent type of synthetic silk makes use of cellulose acetate instead of cellulose or cellulose nitrate. The fibers produced by evaporation or precipitation go under the general name of

celanese and have attained a great deal of popularity since they can be dyed in a large variety of shades.

487 Cellophane

Both viscose and cellulose acetate may be made into thin films of considerable mechanical strength and resistance to water. They are called cellophane and are being utilized as waterproof coverings for all types of materials, including perishable foods.

488 Silk, Real and Artificial

In using the terms *artificial silk* and *synthetic silk* we must be careful to remember that in no sense are these products chemically the same as silk, which, as has been stated, belongs to the class known as proteins. Rather must they be regarded as substitutes, however preferable they may be in many respects to the natural article.

The production of artificial silks has cut into the natural silk industry of Italy, China and Japan to a great extent, especially as the natural material produced in those countries was chiefly for export.

489 Summary

Cellulose may be obtained from the cotton plant or from wood.

The destructive distillation of wood produces methyl alcohol, acetic acid and several volatile liquids useful as solvents. The residue is wood charcoal.

Wood may be finely ground mechanically and pressed so as to give paper. But the chemical treatment involves cooking with calcium bisulfite to rid it of lignin and resins. It may then be bleached with chlorine or a hypochlorite.

Cellulose may be nitrated (three nitrate radicals to each glucose unit) to give cellulose nitrate. This is soluble in some organic solvents and finds use as an explosive—guncotton.

Pyroxylin is a lower nitrated cellulose; with a plasticizer it gives a product capable of molding. Pyroxylin may be dissolved to give collodion and celluloid.

Cellulose forms an acetate which finds use as films, artificial silk, etc.

Artificial silks (substitutes for silk) may be prepared as viscose, Chardonnet silk, mercerized cotton and cellulose acetate.

Cellophane is a thin, waterproof film made from viscose or cellulose acetate.

Questions

1. What are the chief sources of cellulose?
2. Explain what is involved in each of the following: (*a*) sulfite pulp, (*b*) cellulose nitrate, (*c*) pyroxylin and (*d*) cellulose acetate.
3. Classify the various types of artificial silk. What is cellophane?
4. What are the products of the destructive distillation of wood?

35

Catalysis in Industry

490 Theoretical Features

The definition previously given of a catalyst (§ 51) presupposes that a chemical reaction may proceed between two (or more) substances, but that such reaction is influenced beneficially by the presence of an additional substance which appears to take no strictly chemical part in the reaction. In other words, this strict definition does not permit a catalyst to alter the direction of a reaction. A few such cases will be instanced here, but attention is drawn to two facts which seem to qualify this definition. First, a catalyst often appears to influence the velocity of a reaction so tremendously that we tend to wonder if the reaction would proceed at all if no catalyst were added; and, second, if tiny living organisms are to be included among catalysts (and we do so include them) we are forced to admit that they do change the course of a reaction to give products not otherwise obtainable.

The first example given of the use of a catalyst was in the preparation of oxygen from potassium chlorate. The conclusions to be drawn from this experiment are:

(1) The mere presence of the catalyst manganese dioxide appears to demand less energy for the decomposition of the potassium chlorate.
(2) The catalyst is unchanged at the end of the reaction.
(3) The quantity of catalyst is unimportant compared with the quantity of chlorate that can be decomposed with its help.
(4) The decomposition of potassium chlorate can proceed without the catalyst, even if less readily.
(5) The more intimately the chlorate and the dioxide are brought together the better, suggesting some surface importance on account of the large increase in surface when solids are finely powdered.

The above conclusions may be correlated to define a catalyst as a substance which (1) influences the velocity of a chemical reaction, (2) is unchanged at the end of such reaction, (3) is unimportant as regards its quantity, (4) does not of itself bring about a reaction which would not proceed in its absence and (5) appears to depend largely upon its surface for its influence upon the reaction.

Another example is afforded by the manufacture of sulfuric acid by the contact process. Here an intimate mixture of sulfur dioxide and air is passed over a platinum or vanadium oxide catalyst; a rapid union of sulfur dioxide and oxygen takes place. Not all the sulfur trioxide possible is formed, for an equilibrium sets in; but this condition of equilibrium is reached very rapidly in the presence of the platinum.

Again, unless some foreign substance gets in and ruins it, the platinum catalyst can produce sulfur trioxide almost indefinitely. The best results are obtained by using the platinum at its maximum surface, that is, by appropriately spreading it over the surface of, say, asbestos fibers. This reaction thus fulfills all the five conditions previously given for a catalyst.

A third example concerns the decomposition of hydrogen peroxide (§ 50). When dissolved in water to form a 3 per cent solution, the liquid hydrogen peroxide slowly decomposes (equation 7).

To prevent this decomposition so that such solutions will keep, an extremely small quantity of acetanilide ($CH_3CONHC_6H_5$) is added to the solution; this greatly retards the natural decomposition of the peroxide. In this solution the catalyst is dissolved and therefore spread throughout the whole solution—intimately mixed. Here all the five conditions mentioned above are met for the definition of a catalyst, but in this case the reaction is retarded—not accelerated—as in the two previous examples. When a catalyst is used to retard a reaction it is often called an anti-catalyst or negative catalyst. But the correct definition of a catalyst is "a substance that influences a reaction"; this definition includes both acceleration and retardation.

491 Selective Nature of Catalysts

In the foregoing examples the catalysts manganese dioxide, platinum, etc., have been used in different reactions; in other words some substances operate better for certain reactions than for others. That is the rule, and the only exception is that water

would appear to be an excellent catalyst in more cases than any other known substance. But it is found that in many instances not merely one substance only will influence a reaction suitably; other substances may perform the same function even better than the catalyst first used in that reaction. The not too reactive metals (Co, Ni, Pt) are sometimes interchangeable, and one oxide may be as useful as another as long as it is approximately of the same type. On the other hand, some catalysts which work well in certain instances are entirely useless in others because of a certain specific action which they possess.

492 Promoters

Examples are known of two substances used separately as catalysts with moderate success; but when used together the result obtained is far greater than would be expected from the sum of the two effects. Such a phenomenon is called *promoter catalysis*, and the substance added to the original catalyst is called a *promoter*.

493 The Poisoning of Catalysts

This has been observed in several cases, notably in the Haber (§ 494) and Contact processes. In the contact process, when the sulfur dioxide is obtained by the roasting of sulfide ores, traces of volatile arsenious oxide are present in the gas. If these traces reach the platinum catalyst, it ceases to function, and must be removed and rid of arsenic before regaining its catalytic power.

In those cases where an enzyme or other catalyst is at work, for example, in the fermentation industries, poisoning readily occurs and a high temperature is permanently fatal to such catalysts.

Following is a number of catalytic processes not previously described in this book.

494 Ammonia—the Haber Process

This synthesis, credited originally to Haber, is capable of being performed under a variety of conditions and is also known by such names as American, Casale, Claude and Fauser. It is based on the equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 24{,}200 \text{ calories} \tag{172}$$

which suggests that, in this reversible reaction, the liberation of heat and the shrinkage in volume on the right must be evaluated in terms of Le Châtelier's principle. Thus all the methods employed under whatever name stress the importance of operating this process at high pressures (to bring about contraction in total volume) and low temperatures to avoid a reversal to the left. The average conditions are 400°C and 200 atmospheres of pressure (nearly 3000 pounds per square inch). Obviously the large apparatus required to hold large volumes of the gaseous substances involved demands great mechanical strength.

The catalyst employed is ordinarily metallic iron with traces of other metals such as manganese. Under such conditions the yield is about 5 per cent, the ammonia being easily liquefied or dissolved in water, and the unused nitrogen and hydrogen being turned back into the converter.

The raw materials nitrogen and hydrogen may be variously obtained. Where electrical power is cheap, hydrogen may be obtained electrolytically from water, and about one half that used is so prepared. The nitrogen may be obtained from producer gas, a mixture of hydrogen, nitrogen, carbon monoxide and carbon dioxide. By heating this mixture in the presence of suitable catalysts the carbon monoxide is converted to carbon dioxide. If the carbon dioxide is absorbed by, say, limewater, the resulting mixture of nitrogen and hydrogen is very suitable for combining to produce ammonia.

Of the ammonia from all sources, more than one third is utilized in the manufacture of fertilizers, over a quarter is used as the sulfate, about one sixth as the aqueous solution known as ammonia water and about one tenth goes into electrical refrigeration.

495 Nitric Acid—the Ostwald Process

This process depends upon this equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + \text{Heat} \qquad (173)$$

In practice a gaseous mixture consisting of 10 per cent ammonia and 90 per cent air is passed over platinum gauze at a temperature of 800°C. This reaction is very simple, for, being exothermal, it goes on without the addition of heat when once it has started.

The nitric oxide produced reacts with oxygen of the air to give

nitrogen dioxide (NO_2), which dissolves in water to produce nitric acid:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (174)$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \qquad (175)$$

The objection to the use of platinum as a catalyst here is that it is so easily poisoned by phosphine (PH_3), acetylene (C_2H_2), hydrogen sulfide (H_2S), iron oxide dust, etc. More recently the mixed oxides of such metals as iron, bismuth, copper and lead have been successfully tried as substitutes for platinum, since they are not subject to poisoning by such reagents as those mentioned.

496 Organic Catalysts

In the section relating to the digestion of foods in the alimentary system, mention was made of some enzymes whose functions were specific with respect to the foods which they helped to prepare for human assimilation. In other words, each of these elusive bodies, protein-like in nature and yet subject to the same limitations of existence as bacteria, appears to be capable of one job only. The following examples are chosen to illustrate their use in industry.

497 Alcohol from Carbohydrates

Yeast consists of minute plants of the genus *Saccharomyces* and brewers' yeast contains two of these, *Saccharomyces cerevisiae* and *Saccharomyces ellipsoideus.* If starchy cereals, like corn, are treated with the malt amylase diastase, the starch is converted to maltose and thence to glucose:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad (176)$$

Yeast carries the glucose on in a further process of degradation by several stages until ethyl alcohol and carbon dioxide are obtained. If the yeast is now separated from the solution, the ethyl alcohol can be distilled off to the extent desired.

498 Lactic Acid from Carbohydrates

Any source of carbohydrate, such as potatoes and rice, may be treated with diastase until conversion to maltose is complete. This mixture is sterilized by heat to destroy the diastase and then inocu-

lated with an enzyme preparation from sour milk—*Bacillus lactis aerogenes* or *Bacillus aceti lacti*—and kept at about 50°C for a week. The addition of some nitrogenous matter such as bran or ammonium salts is necessary to keep the bacillus active, and chalk is added to keep the solution neutral. The product is calcium lactate, from which lactic acid ($CH_3 \cdot CHOH \cdot COOH$) may be obtained by the addition of phosphoric acid.

A similar use of the *Bacillus butyricus* gives butyric acid ($CH_3 \cdot CH_2 \cdot CH_2 \cdot COOH$); *Bacterium aceti* (found in mother of vinegar) produces vinegar or acetic acid (CH_3COOH), the flavor varying with the kind of fermenting agent used.

Glucose may likewise be made to produce citric acid by the use of certain molds, such as a species of *Aspergillus*. These examples indicate how these acids may be made without depending on the seasonal crops of such citrous fruits as lemons, formerly the sole source of such valuable compounds. Lactic acid is likewise independent of the production of milk. It is noteworthy that prior to World War II, about one half of the potato crop of Poland, formerly the greatest producer of potatoes of all countries of the world, went into fermentation industries.

There are two arresting features of the fermentation industries. First, cheap starchy products and by-products of the sugar industries (cane and beet) may be utilized to provide large quantities of substances otherwise obtainable only from natural products at much greater cost; and, second, in contrast to the advantages implied above, possible contamination and infection by undesirable bacterial growths require special precautions in these industries such as would be unnecessary in ordinary chemical practice.

499 Other Catalytic Processes

The preparation of sulfuric acid has been treated previously. The cracking of petroleum uses aluminum chloride as a catalyst. In the hydrogenation of unsaturated fats and oils, the medium is water, in which finely divided nickel is the catalyst accelerating the addition of gaseous hydrogen to the ethylenic bonds of the fatty acids of the glycerides used. It is a very large industry where vegetable oils, not entirely suitable for public consumption, are hydrogenated to obtain those semi-solids which have been found so satisfactory as a substitute for natural cooking fats. This industry might well be extended to utilize waste fish oils.

500 Summary

A catalyst is a substance added to a chemical reaction to influence its rate. Catalysis may take place by means of contact at a surface or by intermediate compound formation.

Catalysts are selective in their action, aiding some reactions and ignoring others. The surfaces of some catalysts may be prevented from functioning because of impurities, for example, arsenic on platinum. This is called poisoning.

A mixture of catalysts is sometimes extraordinarily reactive—promoter catalysis.

Catalysts may be used to decelerate as well as accelerate a reaction. They really act in such a way as to bring on an equilibrium more rapidly than otherwise would occur.

The contact process makes use of a platinum or similar surface to bring about the formation of sulfur trioxide.

Ammonia may be prepared from nitrogen and hydrogen by heating under great pressure in the presence of iron and similar metals.

The oxidation of ammonia to nitric acid (the Ostwald process) by oxygen proceeds rapidly in the presence of platinum.

Fermentation processes utilize the carbohydrates for the production of ethyl alcohol, lactic, butyric and citric acids and acetone.

Questions

1. Explain what is meant by the term catalysis. What characteristics are usually associated with catalytic action?
2. How may catalysts become poisoned?
3. Are enzymes catalysts?
4. Outline the reactions involved in the Haber and Ostwald processes.
5. What products may be obtained by the fermentation of sugars?
6. Can you name any product made by catalysis for household use?
7. Sketch the kinds of products which may be made using nitric acid (see Part 2).

36

Industries Based on Salt

501 Sodium Chloride

This is the best known of all salts; hence its name *common salt.* Sea water contains nearly 3 per cent of it, formerly washed down from land areas. The Dead Sea and the Great Salt Lake are examples of inland waters with a high concentration of salt. In the United States and Canada there are huge underground deposits of great extent and value.

As a raw material for industry salt ranks high because of the large number of its products. Some of them are presented herewith.

502 Sodium Carbonate—the Solvay Process

This process may be represented as occurring in several chemical stages.

Limestone is heated to give lime and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (177)$$

This carbon dioxide is pumped off and dissolved in water along with ammonia and there reacts to produce ammonium bicarbonate:

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3 \qquad (178)$$

The ammonium bicarbonate undergoes a double decomposition with sodium chloride to produce ammonium chloride and the slightly soluble sodium bicarbonate which precipitates out of the solution:

$$NaCl + NH_4HCO_3 \rightarrow NH_4Cl + NaHCO_3 \downarrow \qquad (179)$$

After being filtered, this sodium bicarbonate is heated, losing water and carbon dioxide:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \uparrow \qquad (180)$$

This gives the anhydrous sodium carbonate, which may, if desired, be dissolved in water and allowed to crystallize out as the hydrate.

In actual practice, however, there are only three stages: the heating of the limestone, the reaction between ammonia, carbon dioxide and sodium chloride and, last, the heating of the sodium bicarbonate.

Sodium bicarbonate is faintly alkaline in solution and is commonly used to neutralize acids. It is a constituent of *baking powder*. Sodium carbonate in crystalline form (hydrated) is known as *washing soda*; it hydrolyzes in water to give an alkaline reaction.

503 The Preparation of Hydrochloric Acid

When solid sodium chloride is treated with concentrated sulfuric acid hydrogen chloride is evolved and sodium bisulfate

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow + \text{Heat} \qquad (181)$$

is left behind. The heat evolved dries off the hydrogen chloride as a gas, which, when dissolved in water to form a saturated solution (about 36 per cent by weight), constitutes the hydrochloric acid of commerce.

To obtain full value for the sulfuric acid used in the process above, a further quantity of sodium chloride on heating releases all the hydrogen chloride available:

$$\text{Heat} + NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl \uparrow \qquad (182)$$

This complete reaction involves heating and therefore additional cost, as well as the production of the normal sodium sulfate.

504 Preparation of Sodium Hydroxide and Chlorine

If a direct current is passed through a concentrated aqueous solution of common salt (NaCl), the chlorine ions tend to collect at the anode and the sodium ions at the cathode. On being neutralized electrically, the chlorine atoms get away as molecules, to be dried and stored in cylinders or utilized *in situ*. But the sodium ions are not set free at the cathode. Sodium being higher in the electromotive series than hydrogen, hydrogen is liberated

at the cathode. As electrolysis proceeds the concentration of sodium and hydroxyl ions increases in the solution. The reaction can be shown as follows:

$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

$$2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$$

and, in solution, with electricity added

$$2Na^+ + 2Cl^- + 2H^+ + 2OH^- + E \rightarrow 2Na^+ + 2OH^- + H_2\uparrow + Cl_2\uparrow \qquad (183)$$

In practice a further reaction is to be avoided, the action of chlorine on the sodium hydroxide if the two are allowed to mix. Consequently, cells have been devised that have a diaphragm separating the cathode from the anode region, this diaphragm permitting the passage of ions but holding the solutions back (Fig. 79). Another type has mercury underlying the aqueous solution and in contact with the cathode chamber, so that the sodium ions are collected by the mercury and, by a rocking motion imparted to the whole cell, are brought to the cathode without coming into contact with the chlorine. Reaction of sodium hydroxide with chlorine produces sodium hypochlorite, which is of course undesirable in the finished sodium hydroxide:

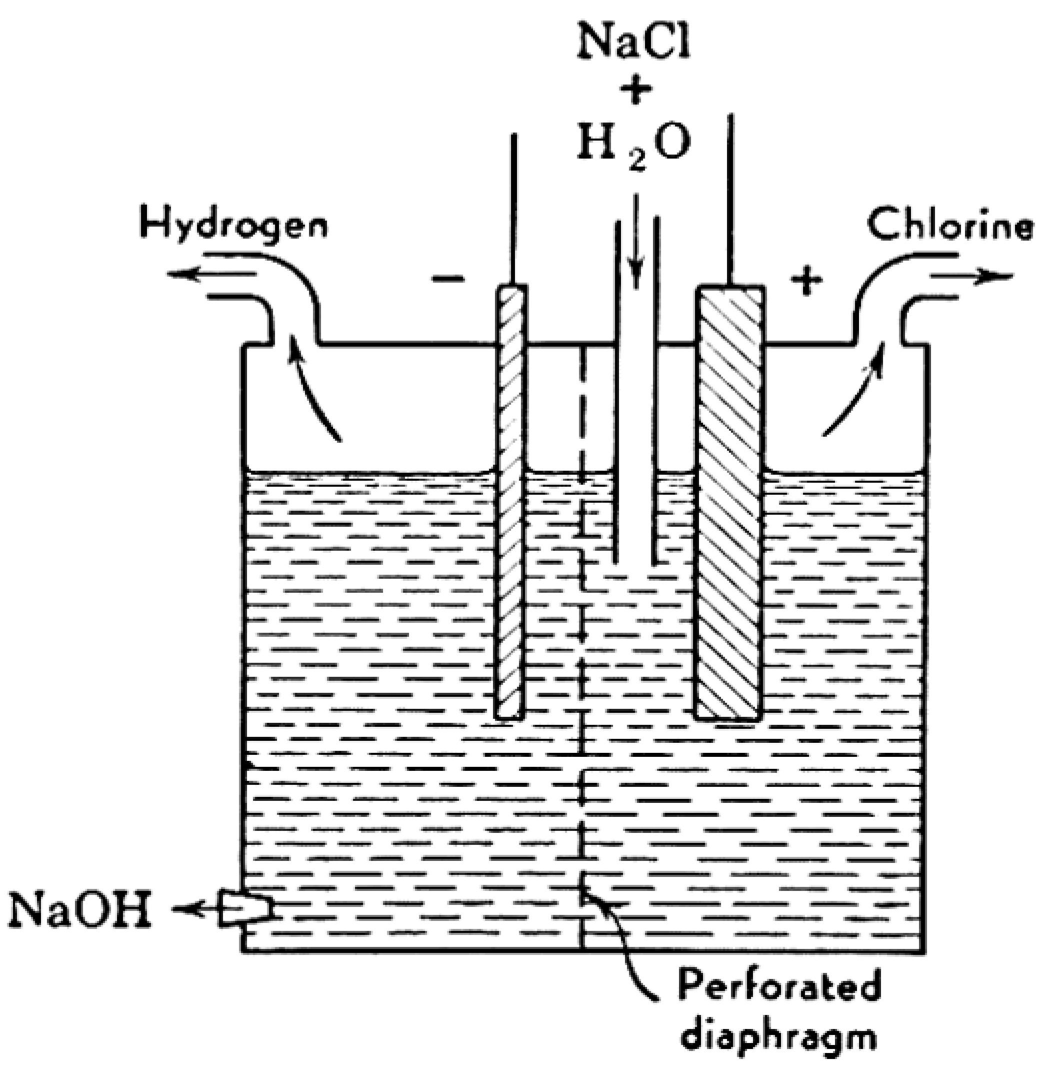


Fig. 79. Diagram of the electrolysis of brine.

$$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O \qquad (184)$$

Eventually the cell will contain aqueous sodium hydroxide. This double preparation of two important inorganic reagents has undergone considerable improvement since its discovery over a century ago and is very successfully operated in both the United States and Canada where common salt and electrical power are both available and comparatively cheap. Some sodium hydroxide is

still being manufactured from soda ash and lime:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2NaOH \qquad (185)$$

but electrolytic chlorine has largely replaced former industrial methods.

One of the greatest uses for gaseous chlorine is in water purification; another is in the bleaching of wood pulp. Aqueous sodium hydroxide is used in the viscose process. The electrolytic method of manufacture permits of partial electrolysis, so that solutions can be prepared containing the required quantities of both sodium chloride and sodium hydroxide wherever such may be demanded.

505 Direct Union of Hydrogen and Chlorine

A generation ago hydrogen chloride, prepared as shown above from sodium chloride and sulfuric acid, was oxidized by passage over a hot catalyst such as MnO_2 or Cu_2Cl_2. This was a commercial method for chlorine. Today this procedure is reversed so that the large amounts of salt electrolyzed have produced a surplus of gaseous hydrogen and chlorine. Consequently, considerable quantities are now made by the union of these two gases. Since mixtures of hydrogen and chlorine explode with violence in sunlight, the reaction has to be carefully controlled:

$$H_2 + Cl_2 \rightarrow 2HCl + 44{,}000 \text{ calories} \qquad (186)$$

This reaction is carried on in a relatively small apparatus of unique design so that a jet of chlorine burns in an atmosphere of hydrogen with the direct synthesis of pure hydrogen chloride. The hydrogen chloride is dissolved in water to produce pure concentrated hydrochloric acid. This very efficient process can produce large quantities of the product.

506 Applications of Electrolysis of Salt

From the three products of this electrolysis further extension is realizable. Should market demands bring about an overproduction of hydrogen, the liquefaction of air will provide nitrogen (§ 59) so that ammonia and nitric acid may be manufactured. Furthermore, the heating of limestone, with its production of quicklime and carbon dioxide, permits of the manufacture of chloride of lime:

$$CaO + Cl_2 \rightarrow CaOCl_2 \qquad (187)$$

Lime and hydrochloric acid form calcium chloride used to settle dust on country roads and provide a brine for refrigeration:

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (188)$$

Sodium hydroxide, treated with chlorine gas, produces sodium hypochlorite (equation 184). The ramifications of such an industry are almost endless.

507 Another Useful Salt—Sodium Nitrate

Sodium nitrate, commonly known as Chile saltpeter, was until recently the chief source of nitric acid. The method is very similar to that used in the laboratory according to the equation

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \uparrow + \text{Heat} \qquad (189)$$

the raw materials being Chile saltpeter and concentrated sulfuric acid. These are mixed in acid-resisting retorts, and the heat liberated is sufficient to drive off the nitric acid as a gas, which is subsequently condensed to a liquid in condensers made of glass, stoneware or some resistant alloy. The remaining sodium acid sulfate will produce another supply of nitric acid, thus:

$$\text{Heat} + NaNO_3 + NaHSO_4 \rightarrow Na_2SO_4 + HNO_3 \uparrow \qquad (190)$$

But this requires such a temperature as would tend to decompose the acid into water and oxides of nitrogen. Consequently, the first stage is that ordinarily employed, the sodium bisulfate being marketable separately.

The resulting nitric acid is 68 per cent pure. When more concentrated it is unstable and slowly decomposes to give water, nitrogen dioxide and oxygen.

Obviously this process is dependent upon supplies of saltpeter which may not be available in many countries; hence the value of the nitrogen fixation methods.

508 Summary

The electrolysis of aqueous sodium chloride produces two substances of great industrial importance, sodium hydroxide and chlorine.

The hydrogen produced at the same time may be combined with the chlorine to give hydrochloric acid.

By the Solvay process sodium chloride can be made to yield sodium bicarbonate and sodium carbonate.

Chlorine is used to prepare chloride of lime, hydrochloric acid, Javelle water and many other compounds of great utility.

Chlorine gas is used in large quantities for water purification and for bleaching.

Sodium nitrate may be used to produce nitric acid.

Questions

1. Compare the electrolysis of sodium chloride in the fused state (Chapter 32) with its electrolysis in aqueous solution.
2. In the electrolysis of aqueous sodium chloride, why is metallic sodium not deposited at the cathode?
3. Compare the methods of preparing hydrochloric and nitric acids from their sodium salts by means of sulfuric acid.
4. (*a*) What is the difference between sodium carbonate and sodium bicarbonate? (*b*) What are some of their uses? (*c*) Can you exchange one for the other in these uses?

37

Ceramics

509 Ceramics Defined

This art stands in much the same relationship to inorganic chemistry as does metallurgy; both are concerned with operations at high temperature. The limits to be assigned to ceramics are in a large measure indefinite. Two principal divisions of ceramics stand out, however. One is classical ceramics, such as the production of pottery, glass and glazes; the other is concerned with refractories and, by extension, Portland cement and slags. In glasses and glazes a liquid is desired which, with a small change in temperature, becomes so viscous that crystallization cannot take place. In the manufacture of refractories and Portland cement the reacting substances become liquid to only a small extent. Throughout the group it is some peculiarity of physical or chemical composition which makes it important.

510 Glass

If pure silica (silicon dioxide, SiO_2) is fused and allowed to cool, a hard, transparent, translucent solid is produced, whose resistance to heat and chemical action (except that of hydrofluoric acid) is very great. Traces of certain impurities may give rise to colored stones of greater or less brilliance similar to the amethyst, ruby, etc., which are all fairly pure quartz, whereas fused silica resembles the natural, uncolored mineral. This fused silica finds large industrial application because of the properties stated above, but it is a fairly recent innovation. About thirty centuries ago glass making was an art dependent upon supplies of silica, though little was done to improve the product scientifically until the nineteenth century. Studies conducted in England and later on in Germany

led to the manufacture of glass of known composition, culminating in Europe in the formerly famous Jena ware.

World War I cut off the supplies of German glass both for chemical and for optical apparatus. But this deficiency actually did not last long, for the American development of glass has produced a product superior in chemical and physical properties to previous types. There are several kinds of glass, depending on the uses for which they may be required, the commonest being window or plate glass, similar to that used in making bottles. This is essentially a silicate of lime.

Ordinary salts of the silicic acids, for example, H_4SiO_4 and H_2SiO_3, may assume a crystalline form on cooling from the liquid state. The presence of an excess of silica (the anhydride of these acids) and other substances, however, prevents this assumption of a crystalline structure. Glass, therefore, may be called a supercooled liquid although it possesses all the other properties of a solid. In time, glasses of certain composition may crystallize out, ceasing to be transparent or translucent, in which case the term *devitrified* is applied to them. Ordinary glass contains sodium, calcium, silicon and oxygen in such proportions as are usually represented by the formula $Na_2O \cdot CaO \cdot 6SiO_2$, that is, with much more silica than would be required for the formulae Na_2SiO_3 and $CaSiO_3$. Such a glass is called a *lime glass*, soda, lime and sand being used in its manufacture.

That each component has a definite effect may be seen from a change in any one of these three. Too much soda makes the glass somewhat soluble (Na_2SiO_3 is water glass), more susceptible to weathering and more brittle; an excess of lime may cause early devitrification; excess of silica raises the melting point. Potassium may be substituted for sodium in whole or in part, in which event the melting point is appreciably raised. Magnesia for lime is a frequent substitution, for with half lime, half magnesia a very satisfactory melting point is produced. Small amounts of alumina promote hardness and resistance to chemical action; arsenic is used to clarify the product.

Modern lime glasses have largely replaced the lead glass of former times, except where lead glass is required for special purposes. The use of boric oxide (B_2O_3) produces the so-called borosilicate glass now so much employed because of its resistance to large

changes in temperature and to chemical reagents. For coloring, various oxides, for example, those of nickel, cobalt, manganese, iron, and the metals gold, copper and selenium, are employed.

The uses for glass seem to be multiplying of late, an extremely fine glass fiber being manufactured for weaving purposes. More recently the manufacture of synthetic resins—organic compounds of high molecular weight—has produced some very fine specimens of material, very light and of excellent translucence, which may in certain instances displace glass, for decorative if not for other purposes. They possess, however, the disadvantages of being soluble in some solvents and of being inflammable.

511 Portland Cement

The use of cement of various kinds for roads and buildings is very ancient. However, modern investigation into the best type of materials to be used in its manufacture resulted, early in the nineteenth century, in a product so similar to the limestone of Portland, England, that it has been named Portland cement. This cement is, like glass, largely dependent on the use of silica, which is combined with the oxides of aluminum and calcium. The whole subject of cement is full of theoretical queries, but it is probably a mixed compound of calcium silicates and calcium aluminates.

Its manufacture entails the heating of limestone and clay in definite proportions until they begin to fuse. This mixture on cooling forms lumps, which are finely powdered and mixed with a small quantity of powdered gypsum (about 2 per cent) to retard the setting of the cement later. When cement is mixed with water, the water is absorbed and some lime is set free, the whole setting to a hard, solid mass. Some natural deposits on this continent contain rocks whose composition is ideal for cement manufacture, requiring merely heating and powdering to produce the required product.

Gypsum ($CaSO_4 \cdot 2H_2O$) may be heated until it loses three quarters of its water of crystallization, producing the well-known and long-used plaster of Paris ($CaSO_4 \cdot \frac{1}{2}H_2O$). On being mixed with water, plaster of Paris forms a fine finish when ultimately solidified. It is used in interior decoration and for many other purposes, including plaster casts in surgery.

512 Porcelain

The principles which govern the manufacture of glass and to some extent that of Portland cement are important in the production of porcelain, chinaware, brick, tile, etc. Kaolin, or china clay, is formed by the weathering of feldspar, and is a hydrated silicate of aluminum such as may be approximately expressed by the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. When mixed with other substances such a silicate is called a *clay*. Clays differ considerably in composition, but one which will form a plastic mass with water can usually harden considerably at about 1100° or 1200°C. Thus various objects can be made of wet clay, mixed with salts of potassium, calcium, etc., suitably molded by hand or otherwise and fired, to produce anything ranging from bricks to fine chinaware. If this porous solid is dipped in a creamy suspension of feldspar and silica and again fired, the metal salts aid in producing a lustrous coating of silicates, which when molten enter the pores of the original object, making it waterproof—glazing. A somewhat similar process is involved in coating cast iron for making enamel sinks, bathtubs, etc. The partial vitrification of china and porcelain reaches its maximum in glass.

513 Summary

Ceramics is the name applied to the making of pottery, glass, etc.

Glass is a complex compound of silicic acid and calcium, sodium, etc., in which an excess of silica prevents crystallization and gives a transparent, translucent product.

Most glass is made from lime, soda and silica. Varying the components produces a hard or soft glass at will, which may be colored according to the ingredients added.

Portland cement is made from silica, alumina and lime; to this a small quantity of gypsum is added to delay the setting that ensues when water is added to the powdered cement.

Porcelain is made from kaolin or china clay. Suitable firing produces a hard mass, which, when treated with feldspar and silica and again fired, becomes coated with a silicate glaze.

Questions

1. What materials are included in ceramics?
2. What raw materials enter into the manufacture of glass? How do they affect the kind of glass obtained?
3. To what use is glass now put?
4. What is porcelain?
5. Of what advantage is a glaze?
6. Why is gypsum used in the manufacture of cement?

38

Petroleum

514 Petroleum History

Although the soldiers of Alexander the Great noticed oil oozing out of the ground in their march across Persia, the history of the utilization of petroleum began in 1858 in the United States of America. Until recent years petroleum could not be called so distinctly chemical in its many ramifications as could either wood or coal; rather was it a source of power, and this it continues very largely to remain. But in the ninety years since the accidental discovery of an oil well in the eastern United States, this complex mixture of many hydrocarbons has come to enjoy a measure of importance which, in its international scope, takes precedence over all natural resources except gold and iron. Indeed signs are not lacking that oil resources are of great international importance and will continue to be for many years to come.

The composition of petroleum deposits varies rather widely and according to the source. Some contain relatively large proportions of gaseous hydrocarbons; others are at the other extreme and are asphaltic in nature. Where the supply of gas is sufficiently large, it can be piped long distances to serve the same purpose as coal gas in city heating.

The crude oils may vary in fluidity from limpid liquids to hard asphalt-like masses. They may be classified according to their content of (1) paraffin waxes and (2) asphalt. Where the content of waxes is high and the content of asphalt low we may expect to obtain a good yield of gasoline, etc., and lubricating oil. If, however, the asphalt content is high and the wax content low, the result is more suitable for liquid fuel, and the asphalt residue after distillation is utilizable for waterproofing and road building. Within the United States the crude oils of Oklahoma and the Gulf Coast

show a high content of light oils such as gasoline; those from Pennsylvania yield excellent lubricating oils; those of California are higher in asphalt. Mexican and Venezuelan crude oils are largely asphaltic, the Mexican containing much sulfur. Oils from the Baku district in Russia, from Iran, Rumania, Burma and Formosa are of the gasoline and kerosene type largely. Russian oils contain considerable proportions of naphthenes—cyclic hydrocarbons of the cyclohexane type; they have in some instances a medicinal value.

515 Production of Petroleum

To obtain petroleum from its subterranean beds, holes are drilled through the rocky coverings. Frequently when oil is struck the outrush of gas is so violent as to require some time before the exit can be capped so as to drain the well at leisure. Much of the gas so evolved is lost to the atmosphere, though the helium content is important enough in some instances to justify its separation. The gases issuing from some types of petroleum deposit contain hydrocarbons of the methane family and may be piped away to large centers of population to serve as domestic fuel.

Where oil wells are at some distance from the point of distribution, such as an ocean port, it may be wise for several reasons to build a pipe line from the well to the port. Crude oils are usually viscous and especially so in cold weather. Such conditions require pumping into the line under considerable pressure at the well end. If the line is a long one, various force pumps may be required en route to continue the flow of liquid. Incidentally, the engineering features are noteworthy in that today the pipes are usually twelve inches in diameter and welded together. Moreover, the storage of huge quantities of oil has required especially strong tanks with adequate precautions against fire.

The preliminary refining of crude petroleum is essentially a physical operation, the mechanical separation by distillation of various fractions according to selected temperature ranges. For example, the liquid distilling over up to 80°C is called petroleum ether; between 35° and 200°C, gasoline; 200° to 300°C, kerosene, etc. Above kerosene come the fuel oils, and by later treatment various semi-solid and solid materials are obtained—paraffin waxes, etc. This process of distillation removes the volatile components and leaves residues, that is, it is a mechanical separation of the

actual components already present. But if the less volatile residues are heated under pressure, the larger molecules of which these residues are composed are broken down by heat into smaller ones, that is, into those of the same kind as those which were volatilized in the lower fractions. This process is called *cracking*—a very suitable name for what actually occurs. That this cracking is possible was known to Dalton and Faraday and was advocated by Silliman in 1855. It is now a well-recognized procedure for working up less valuable residues into the volatile gasoline so much in demand by the automotive industry.

The consequences of large-scale cracking are many. Ethylene and other compounds of its type are produced and are now extensively utilized for preparing ethylene glycol, synthetic rubber and a variety of solvents new to industry. Moreover, cracking produces some hydrocarbons of the benzene type which are less likely to knock [1] than a fuel composed entirely of straight-chain paraffins.

The hydrogenation of the heavier oils under pressure improves the quality of such oils for lubrication purposes.

The process of distillation is not alone sufficient to purify petroleum, for quantities of sulfur compounds and gums are deleterious in their action on the metal surfaces of engines, bearings, etc. Washing with sulfuric acid in small quantities removes much of the gum and discoloring matter, and the subsequent use of sodium hydroxide solution neutralizes any residue of acid and also removes the compounds of sulfur. Other methods of treatment are variously employed for special purposes.

Although natural gas is about nine tenths methane and one twentieth the low paraffin hydrocarbons such as ethane, propane, and butane, there are, besides them, helium, nitrogen and carbon dioxide. But, though the percentage of the latter substances is small, their quantity is very large since the quantity of natural gas is of enormous proportions. Today, by refrigeration methods, butane is liquefied from this escaping natural gas and put up in cylinders under pressure for household use in regions where other sources of heat are not available.

[1] Knocking is the name applied to the abnormal explosion of a fuel-air mixture, which, in a high-compression, internal combustion engine, is indicated by a knocking sound in the cylinders and is disadvantageous to efficient operation.

516 Summary

Petroleum and natural gas are the residue of former animal life. Deposits are widely dispersed in the world.

Petroleum deposits are of two main types, paraffinic and asphaltic. Their use in industry depends upon the type.

Petroleum oils are separated by distillation into fractions of varying usefulness. Residues may be *cracked* into smaller molecules to increase the more useful products of the industry.

The economic importance of petroleum is enormous. (Readers should consult advanced textbooks on this subject because of its international importance.)

Questions

1. What is the importance of petroleum distillation? What is "cracking"?
2. Name the various petroleum products with which you are familiar, and state their uses.
3. Write a page on what you believe to be the position of North America in petroleum self-sufficiency.

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Polymers and Plastics

517 Polymerization

A phenomenon observed mainly among carbon compounds is the union of two or more molecules of the same substance to produce a new compound. It may be represented thus:

$$3CH_3CHO \rightarrow C_6H_{12}O_3 \tag{191}$$

where three molecules of acetaldehyde unite by the acid of a catalyst to form a single molecule of paraldehyde. This union of a number of molecules to form a single molecule of a new compound (1) without the loss of any atoms, (2) with the same percentage of constituents and (3) with a multiple molecular weight is called *polymerization*. This kind of reaction is very common among compounds which possess doubly bound atoms such as carbon or oxygen, or both, but more particularly among the ethylenic hydrocarbons. Should sufficient molecules take part, the resulting products have high molecular weights. The majority of common compounds possess molecular weights of less than 1000. High polymers, as they are called, show molecular weights in the tens and hundreds of thousands. Examples of such polymers produced in nature are starch, cellulose and resins. Cellulose may be chemically modified to produce cellulose nitrate or acetate, both of them of high molecular weight.

Molecular weights are not in themselves important. What is of importance is that such high polymers possess special physical properties. High polymers are easily recognized. Whereas compounds of low molecular weight are gases, or mobile liquids or crystalline solids, high polymers are either viscous liquids or amorphous solids. The unique physical properties that the high polymers possess are of the type we call mechanical, such as tensile

strength, flexibility and elasticity. The existence of such mechanical properties in high polymers is of fundamental importance in human betterment. It can be stated with assurance that, if we find a high polymeric substance in nature, or if we synthesize one in the laboratory, it will be found to be either a flexible rubber, a moldable plastic, or a spinnable fiber. In addition it may show useful adhesive and film-forming properties. There is no need to stress the importance to modern civilization of such diverse products as rubbers, plastics, textiles, adhesives and protective coatings.

If we investigate the molecular structures of high polymers we find that they belong to one of two classes. Either they possess (1) long, chain-like molecules or they possess (2) three-dimensional, lattice-like molecules.

Theory and experience agree that chain-like molecules exist in a kinked-up or even a coiled-up condition; thus each molecule functions like a coiled spring. Lattice-like molecules can be formed from a number of chain-like molecules by cross-linking—not unlike a bedspring. When this happens a very large molecule is obtained which is insoluble and infusible. It is thus possible to build up a large number of synthetic resins not unlike natural resins, but with more predictable properties.

We are not, however, restricted to the polymerization of a single compound. Mixtures of compounds can be "co-polymerized" to form products of high molecular weight and valuable physical properties; this type of reaction is called *polycondensation.*

The vinyl polymers and acrylic esters have properties of interest as insulators and optical instruments.

A number of commercial resins of the polycondensate type is listed here:

(1) Alcohol-acid resins, the *alkyds.* The equations for their formation were given above. The alkyds are widely used in paints and varnishes, and their use made possible the so-called four-hour enamels.

(2) Amine-acid resins, the *polyamides.* The nylons, the new synthetic fibers so widely used as substitutes for silk in parachutes and in stockings, are *superpolyamides.*

(3) Phenol-aldehyde resins, the *phenolics.* Bakelite is a phenolic. It was the first of the synthetic plastics and remains the most popular for molding, such as in hand grenades and

land mines. In another form it makes a most durable adhesive for plywood, especially for boats.

(4) Amine-aldehyde resins, the *ureas*. The ureas also are used in molding compounds, as for uniform buttons and shipboard tableware, and as a cold-setting adhesive for assembly work, as in the so-called *plastic planes*.

(5) Halide-sulfide resins, the *thiokols*. These polymers are oil-resistant synthetic rubbers.

518 Plastics

These are synthetic resins which can be molded into various shapes under heat and pressure and so produce stable forms. Plastics are generally resistant to chemical action, of low specific gravity and electrical conductivity and can be produced in colors. They may be transparent or translucent or opaque. In many instances they may be used to replace metals, but they all lack the hardness and strength of metals.

Resins are divisible into two main types which are related to the degree of cross-linking in the polymer lattice, the *thermoplastic* and the *thermosetting*. The former are relatively soft to abrasion, flexible under stress, fusible on heating, and soluble in solvents to form colloidal solutions. Thermosetting resins undergo a "cure" when heated; the number of cross-bonds is greatly increased. A cured resin is relatively hard, brittle, infusible and insoluble.

It is possible to modify the nature of natural polymers and to control the nature of synthetic polymers so that rubbers, plastics, or fibers can be obtained at will. This is a fact of great economic and social importance. The modification of the natural polymer, cellulose, will serve as a good illustration of the technique. Cellulose as it exists in cotton or in wood contains highly orientated molecules which are maintained in this state by strong cross-links involving the many hydroxyl radicals present. If these hydroxyl groups are chemically modified (as by the formation of acetate) these cross-links are weakened; such cellulose esters are thermoplastic. If these are still further modified by a physical process, for example, by dissolving in a minimum of high boiling solvent such as castor oil, the cross-linking is further weakened and the "plasticized" cellulose esters become rubber substitutes. The reverse of this process is exemplified by the vulcanization of rubber (a hydrocarbon polymer) and the drying of paints.

Thermoplastic resins oftentimes contain plasticizers which render them more fluid during the molding process and more flexible after molding. Thermosetting resins always contain fibrous fillers. They would be too brittle without them. These fillers vary widely, depending upon the end in view. One of the most common of them is wood flour. It is a general purpose filler for thermosetting resins which are to be molded. A mineral filler, such as asbestos, has the additional advantages of increasing the abrasion resistance, the heat resistance, the chemical resistance and the electrical resistance of the resins. If mechanical strength is at a premium, fillers which possess "structure" are used. Sheets of paper, of wood, of cloth are saturated with resin and then cured with heat and pressure, not in a closed mold, but between the flat plattens of a laminating press. Recent research has indicated that resins filled with woven glass fiber have phenomenal tensile strengths approximating that of steel. There is one disadvantage in such "structures" fillers. They decrease the flow of the resin and, when used, the resin cannot be molded into intricate shapes but only laminated into sheets of simple curvature.

Natural fibers are usually spun, woven and used in their natural form. Synthetic fibers are processed. This processing has for its purpose an increase in the orientation of the chain molecules so that as far as possible they will lie along parallel axes and the strength will be at a maximum. Weight for weight, such orientated fibers may have tensile strengths far in excess of the finest steel. There are several methods of accomplishing the required "orientation." Two methods commonly practiced are (1) to extrude a solution of the high polymer through a very fine orifice or spinnaret into a precipitating bath and (2) to stretch or "cold draw" a fiber to three or four times its original length. It should be remembered that such orientation is a reversible process, and is reversed by the agency of heat, or solvents. The fiber reverts to a plastic. Some of us remember with chagrin the disastrous effects of pressing one of the modern synthetic textiles with too hot an iron, or of dropping on it some nail polish remover.

Many people with more imagination than insight often suggest that plastics are the answer to all our technological problems. This is not so. A number of resins are manufactured and many more can be synthesized, but any one of them has and will have its advantages and its disadvantages. There is no perfect resin.

519 Summary

Polymerization is the union of several or many molecules by repeated additions to give a product of high molecular weight and notable physical properties.

The synthesis of a molecule of high molecular weight by repeated condensations with the appearance of a by-product is called polycondensation. The results of both kinds of reaction are similar.

Plastics are moldable resins of two main types, the thermoplastic and the thermosetting.

The physical properties of synthetic resins are determined (1) by the radicals of the molecules involved and (2) by the type of product, whether chain-like or lattice-like.

Chemical and physical modification of resins produces a very wide variety of properties and hence of commercial uses.

Questions

1. Define polymerization and polycondensation.
2. What is a plastic?
3. What is a plasticizer?
4. What is the difference between "thermoplastic" and "thermosetting"?
5. How does chemical structure confer physical properties in synthetic resins?
6. Give any examples you can of the use of resins.

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Chemistry in the Home

520 The Show Place of Chemistry

A little thought given to the content of this book must impress us with the important role which chemistry plays in our everyday life. If we leave our minds open to the impressions which crowd in on us in our daily tasks we become more and more aware of this role and also of the parts played by other branches of science. Thus we gain an insight into what appears to be an orderly plan constantly developing around us. Although we are, in a material sense, part of that plan, our powers of thought enable us here and there to aid in its direction. Should our aid be in the direction of helping mankind to achieve its highest objectives, our contribution will have been worth while.

Since the family is the unit of our civilization, it is to be expected that the home will contain the greatest diversity of materials supplied by industry of all kinds. That this is so can be appreciated as we look around the average home. The building will show evidence of cement, plaster of Paris or treated wood. The paint, varnish, lighting fixtures, curtains, draperies, ornaments, fuel, heating equipment, medicine cabinet, kitchen shelves—all these show evidence of chemical processing to a greater or lesser degree. In addition to this evidence, it is in the kitchen that the procedures of chemistry are practiced with a greater dependence on scientific methods than is generally realized. The practical effects of temperature, pressure and catalysis were known centuries before they were explained. Part 3 of this book treats of foods in relation to digestion and value in assimilation. The rest of this chapter is devoted to the explanation of the chemistry of food preparation.

521 Cooking

The word *cooking* includes all the procedures that the cook employs in preparing a meal. Although the making of a sherbet is one of these procedures, the more specific application of the word is to those culinary acts which involve heat at some stage.

Cooking is a complex procedure because it involves preservation, digestibility, enhancement of flavor and texture of the finished product. These factors will become evident as we proceed.

522 Bread, Cake, Pastry

Wheat flour, whether refined or not, consists of starch with smaller quantities of gluten and protein. Without this gluten, the flour particles would not adhere in the loaf. When water and flour are first mixed the presence of gluten is shown by thin, sticky strands which hold the starch particles inside them. The more this dough is mixed, the more these fine strands tend to adhere, becoming less sticky and more elastic. It is the development of this elasticity which allows (1) much starch and fat to be held together and (2) much carbon dioxide gas to be retained. Too much kneading of the dough tends to prevent leavening, that is, dissemination of gas.

In bread, carbon dioxide is supplied by yeast, which ferments a little of the starch and produces carbon dioxide bubbles and some flavor. Obviously, if the dough is too wet, the gas will not be retained during baking. Consequently there is an optimum consistency of the dough which will make for satisfactory "rising" without "falling."

Baking is designed to destroy the yeast, "set" the gas bubbles and remove excess water. Consequently the oven should be hot at first and cooler later on. The finished product is a colloidal solution (although solid) of carbon dioxide dispersed in starch with gluten as the protective colloid (see Chapter 15).

Cakes may contain eggs, fat, flavoring and other ingredients. Here again we are dealing with a colloidal mixture in which gluten is essential to "protecting" the dispersed particles. The condition of the gluten is most important in that it must not be "overdeveloped," that is, stirred or kneaded too much. Egg white, another protective colloid, helps to protect the structure of the finished product. But fats need much protection to prevent separating out, with consequent greasiness after baking.

A more rapid source of carbon dioxide than yeast is either sour milk or cream and baking soda, or a prepared "baking powder." The soda is mixed with the dry flour to obtain uniformity of distribution; the sour milk or cream is added towards the end of the mixing. The cake is then ready for baking. Rising is produced by the interaction of lactic acid and soda:

$$CH_3CHOHCOOH + NaHCO_3 \rightarrow CH_3CHOHCOONa + H_2O + CO_2\uparrow \quad (192)$$

Too hot an oven may cause the carbon dioxide to leave the dough before the cake has set.

Prepared baking powders depend for their use on the evolution of carbon dioxide. The earliest of them was made of sodium bicarbonate and potassium hydrogen tartrate ("cream of tartar"). Their reaction is

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2\uparrow \quad (193)$$

They need careful measuring, for too much cream of tartar affects the flavor of the cake. If too much soda is used, it decomposes on heating to give Na_2CO_3 (washing soda) as in the Solvay process. This sodium carbonate will tend to saponify any fat present to form a soap, which again ruins the flavor of the cake.

To obviate the difficulties of measuring the ingredients, prepared baking powders of standard strength are readily available. They are of three general types: (1) tartrate, (2) phosphate and (3) alum. All contain sodium bicarbonate to supply carbon dioxide. Starch is added to prevent deterioration by moisture and to insure the correct amount of gas for a definite volume of powder no matter what brand of powder may be used. Deterioration is shown by the formation of lumps in the powder and is caused by not keeping the container tightly closed.

Type 1. It has been mentioned previously and its reaction given by equation 193. Tartrate powders given off carbon dioxide rapidly and in cold mixtures.

Type 2. This type contains calcium acid phosphate. The liberation of gas is shown by

$$NaHCO_3 + Ca(H_2PO_4)_2 \rightarrow CaHPO_4 + NaH_2PO_4 + H_2O + CO_2\uparrow \quad (194)$$

These powders are slower in their action than type 1.

Type 3. These powders contain alum and react as follows:

$$Na_2SO_4 \cdot Al(SO_4)_3 + 6NaHCO_3 \rightarrow$$
$$6Al(OH)_3 \downarrow + 3Na_2SO_4 + 6CO_2 \uparrow \quad (195)$$

They require the batter to be hot before delivering gas. Most powders of this type contain some calcium acid phosphate so that their effect is that of types 2 and 3 combined. Each type has its own particular advantage, especially if the batter is to be cooked at once, like cake batter, or to stand awhile, like pancake batter.

Sometimes powdered egg white is incorporated into the baking powder. It helps the batter to retain the gas a little longer.

After cooking has been completed, each type of leavening leaves its own residue, as shown in the preceding equations. These residues differ somewhat in taste. Their quantity, however, in any case, is small, and none of them has any harmful effect.

523 Meat

Meats of all kinds are composed of muscle fibers enclosed in a sheath of *connective tissue.* This tissue, quite noticeable in beef muscle, resembles the cellulose coating of grains. Inside this sheath are small quantities of fats, but mainly digestible proteins. Red meats also contain hemoglobin. During storage certain changes occur by enzyme action which tend to soften the protein and render it more soluble in the digestive fluids.

A great variation exists among the muscle fibers of different animals, but it is of particular importance that beef be hung for at least a week in a cool place. This hanging softens the tough connective tissue, and the low temperature prevents undesirable enzyme and bacterial action.

The cooking of meats by whatever method must take into account the connective tissue, which is composed of two proteins, *collagen* and *elastin.* Neither of them is soluble in water, but collagen is converted to soluble gelatin by hot water, particularly in the presence of acid or alkali. Elastin is insoluble and is present in old or much used muscles. In rib beef the collagen and elastin are nearly equal in proportion, but the elastin is twice as great in beef shank. Pork and chicken contain only small amounts of each with a very small proportion of elastin.

Coagulation of meat proteins occurs as low as 60°C (104°F), and moist heat is more favorable to the conversion of collagen to gelatin than dry heat. In general, then, tough cuts are rendered more digestible by stewing or pot-roasting. But the various temperatures and times employed by experienced cooks are largely a matter of individual choice.

Fish have as a rule much less connective tissue than land animals and they are similar in this respect to poultry. Curing always tends to soften these tissues whether they are beef or fish, besides aiding in the coagulation of the protein; curing is really a form of cooking.

524 Vegetables and Fruits

There is tremendous variation in the composition of vegetables and a similar variation in the effects of cooking. Starches undergo dextrinization, vitamin C may be destroyed, crude fiber may be partially hydrolyzed, vitamin B may be washed out by boiling in a large volume of water and a great proportion of the flavor may volatilize. Most ripe fruits and many vegetables are better uncooked. But if we have been brought up on cooked vegetables, we tend to prefer them. Cooking by waterless and by pressure methods is less wasteful of food value, as a rule.

The inorganic or mineral salt content of fruits and vegetables is probably even more important than the vitamin content and is not destroyed by cooking unless washed out by long boiling in too much water. The cooking time varies according to the kind of food, the type of cooking, the utensil used (open dish, waterless covered or pressure), the kind of finished product and the condition of the food. All these factors have to be considered by every student of the science of cooking. This fact is well illustrated in canning, particularly in the destruction of enzymes or bacteria which might cause spoiling of the product. Here both the time and the temperature are important. For example, a fruit which is appreciably acid is sterilized very rapidly at the boiling point. On the other hand, the non-acid foods, like most vegetables and meat, require a much longer time at a higher temperature. In other words, the rate of sterilization is directly proportional to the hydrogen ion concentration of the medium.

For more nearly complete information on the chemistry of cooking, the reader is referred to several standard textbooks which

cover every phase of the subject. The principles which apply to chemical reactions in general are found to be the same as those which apply to chemistry in the home.

525 Summary

The cooking of bread, cakes and pastry involves the formation of a colloidal mixture of starch granules, protein and fat, together with a leavening agent which produces carbon dioxide. They are protected by gluten to produce the desired texture of product.

Leavening may be brought about by one of two general methods. The first uses yeast and produces fermentation of some of the starch, with consequent formation of carbon dioxide. The second method involves a chemical reaction between sodium bicarbonate and a weak acid such as lactic acid, or cream of tartar, calcium acid phosphate or alum.

Prepared baking powders, of the second type, are designed to produce results suitable to the kind of cooking required.

All animal muscle connective tissue contains collagen and elastin to different extents. It is on them that cooking methods of meat and fish are concentrated.

Vegetables vary greatly in their constituents, and their cooking depends upon a large number of factors.

Questions

1. What are the chemical reactions which cause bread and cake to rise when baking?
2. How may the temperature and the type of baking powder affect the rate of evolution of carbon dioxide?
3. Compare collagen and elastin in their reaction to attempts to hydrolyze them.
4. Why do acid fruits and vegetables usually require a cooking time different from that of the non-acid kind?

BOOKS FOR SUPPLEMENTARY STUDY

These are suggested as an aid to the instructor when the interests of the class require more extensive information.

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